Chapters on papermaking ...

Clayton Beadle

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Chapters on Papermaking

VOL. I.

COMPRISING A SERIES OF LECTURES DELIVERED ON BEHALF OF THE BATTERSEA POLYTECHNIC INSTITUTE IN 1902.

BY

CLAYTON BEADLE

Lecturer on Papermaking
before the Society of Arts, 1898 and 1902;
at the Papermakers' Exhibition, 1897; at the Dickinson
Institute, on behalf of the Hertford County Council, 1901, and at the
Battersea Polytechnic Institute, 1902; awarded the John Scott Legacy Medal
and Premium of the Franklin Institute by the City of Philadelphia,
and the Gold Medal of "La Société pour l'encouragement
de l'Industrie Nationale" of Paris, and
other Medals and Awards.

LONDON
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1907

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By CLAYTON BEADLE,

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PREFACE.

This small contribution to the subject of Papermaking consists of a reprint of the ten Lectures prepared on behalf of the Battersea Polytechnic Institute in 1902, the right of publication of which was reserved to the Author.

These Lectures appeared in the columns of PAPER AND PULP. Many of the readers of that Journal having expressed a desire to have them for reference, the Author determined to reprint them in book form.

Papermaking, like other progressive industries, is undergoing changes: what is new to-day will be old to-morrow; and lectures on Papermaking must share a similar fate; but the subjects with which these lectures deal will remain with us, and will continue to engage the attention of the Papermakers and Papermaking Chemists of the future.

CLAYTON BEADLE.

Laboratories: 15, The Boro',
London Bridge, S.E.
March, 1904.

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LECTURE I.

EXAMINATION OF FIBROUS RAW MATERIALS FOR PAPERMAKING.

Moisture—Ash—Cellulose—Non-cellulose—Chemical behaviour—Yield—Commercial value—Consumption of chemicals—Chlorination—Precautions for treatment—Rag examination.

It will be noticed on looking at the syllabus of these lectures that there is no mention made of this subject. The fact is that the syllabus was only intended to give a general statement of some subjects, as a rough guide, which might be treated of in this course of lectures. For future lectures I shall have to be guided largely by the composition of the class, and the requirements of the students who attend. This I hope to discover during the half-hour devoted to discussion on the lecture.

I have long ago given up all attempt to deal with the subject of papermaking in a general sort of way, as it is generally dealt with in text-books. I do not think it advisable to attempt to give an elaborate and detailed description of the processes as they follow one another in the ordinary course of papermaking, such as is attempted in Hoffman's Treatise and other text-books dealing with the subject from a general point of view.

It is impossible for anyone to become a papermaker, or to acquire a practical knowledge of papermaking, merely by listening to lectures or by studying publications on the subject; but it should be possible for students to obtain a more intellectual grasp of the subject, especially if they are engaged in a paper mill.

I understood that this class would consist partly of students engaged in paper manufacture and partly of students engaged in large stationery businesses who desire to get a closer knowledge of the paper which goes through their hands. I cannot hold out any hopes that the latter will ever be able to consider themselves papermakers, however much they may study the subject. In

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order to understand the manufacture of paper, and to be of real practical service in a paper mill, it is necessary, of course, to go through the mill, working in each of the chief departments. This, however, is only the privilege of the few who are likely to become foremen and managers of paper mills; the majority have to be contented with a more limited experience. It is possible, however, that an ordinary workman may go through one department to another, as opportunities arise for his promotion.

I have always claimed that it is important for any workman to have some knowledge of the actual mechanical operations which he may have to conduct in his ordinary routine work, and also of the operations which are affected by his own labour. This I endeavoured to emphasise in my lecture before the Society of Arts. I regard this as particularly true of papermaking. In many of the departments a man's work is largely dependent upon the work of other departments. As an instance of this, I would mention the way that the work is done in the rag-house will affect that process right throughout. The beating also has an important effect upon the way the material will work upon the machine. It is important for the machineman to know something, at any rate, about beating; and it is important also that the beaterman should know something about the way the treatment of the fibres in the beater influences the stuff as it passes over the paper machine, in order that he may beat his stuff to the best advantage for the machineman.

It is evident that the large stationers of this country who are engaged in the selling of paper desire that some of their staff should possess some knowledge, at any rate, of the process of papermaking and the composition of papers. It appears to me that this may be carried too far. Taking a more broad-minded view, I think, on the whole, it would be more to the advantage both of the papermaker and the stationer if they knew something about the difficulties with which they each have to contend, and without trespassing on each other's domains. This might be done in some measure by the holding of classes where practical subjects are discussed.

I have chosen for the subject of this evening's lecture the preparation of fibrous raw materials. I think it is a subject which should prove of a good deal of general interest. The information which I have to put before you may be rather in advance of some of the students in the class, but as the lecture is to be printed in the columns of PAPER AND PULP, they will have opportunities of studying it at their leisure, and to ask me

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questions in regard to same during the discussion after subsequent lectures.

If any of those who take notes of these lectures desire to ask any question which deals directly with the subject of the lecture, I should be obliged if they would briefly state their question in writing, that I may endeavour in a future lecture to give them information on the question which they raise, or, if time is short, to refer them to some means of obtaining information through some publication bearing on the matter.

The examination of fibrous raw materials in a systematic way is outside the province of an ordinary worker, and such work requires a good deal of experience and special appliances; but it is instructive, as, in order to examine the raw material, it is often necessary to put it through treatments and processes more or less imitating what takes place in the paper mill. By the results obtained from such treatments and processes, a very fair practical knowledge can be obtained of the quality and value of the fibres under treatment.

As far as I am aware no systematic attempt was made in this direction until the Indian and Colonial Exhibition in 1886. My cousin, Mr. E. H. Joynson, at whose mill I was at work at the time of this Exhibition, was very anxious to undertake, in conjunction with the well-known chemists, Messrs. Cross & Bevan, a systematic examination of the fibres exhibited at this Exhibition. This was finally arranged at a conference held at the Exhibition, and I was deputed by Mr. Joynson to carry out the analytical work in conjunction with Messrs. Cross & Bevan, of London. This work lasted about six months. As a result a special report was issued by the authority of the Secretary of State for India, dealing with the various Indian fibres, and a further report was issued by the Colonial Secretary, edited by Sir Henry Trueman Wood.

I give you here, from the Indian report above mentioned, the *modus operandi* adopted for the examination of the various fibres, or the determination of—

Moisture,
Mineral constituents,
Hydrolysis,
Cellulose,
Mercerisation,
Acid purification, &c.

"MOISTURE.—All the celluloses hold, in their ordinary state, a certain proportion of moisture, or as we may term it, water of condition, which

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within the limits of variation (1–2%), due to atmospheric changes, is definite and characteristic of each fibre. It is noteworthy that the proportion of hydroscopic moisture is an index of susceptibility of attack by hydrolytic agents; it is certainly true that the textile fibres of the highest class are distinguished by their relatively low moisture. The extent to which this condition is applicable will be seen by an examination of the table of analytical results.

"It is scarcely necessary to say that the moisture is determined by drying a weighed quantity of the fibre. It is necessary to raise the temperature to 110 degrees (C.) to drive off the whole of the water. At 100 degrees a fibre will often retain 1% of its weight. Owing to the variations in this constituent, it is expedient to express all the results of analysis as percentages of the dry fibre.

"MINERAL CONSTITUENTS.—The ash left on incinerating the fibre is determined in the usual way. The proportion is low in the ligno-celluloses, higher in the pecto-celluloses, and especially when the proportion of non-cellulose is high. Cellular tissue further contains a higher proportion of mineral constituents than the fibres, and an admixture of the former, therefore, raises the percentage.

"HYDROLYSIS.—There are two classes of reagents which intensify the resolving action of water upon organic bodies known as hydrolysis, they are the acids and alkalies of these. The former, for the most part, exert a very destructive action upon the vegetable fibres, and though the study of this action would doubtless afford valuable information, it has not been found expedient to include it in our scheme of analysis.

"The action of boiling dilute alkalies, on the other hand, effecting a simpler resolution, and involving very important points in the practical applications of the fibres, gives results which form a necessary part in their diagnosis. A convenient, though of course arbitrary method, has been selected as follows:—The fibre is boiled (*a*) for five minutes in a solution of caustic soda (1 per cent. Na_2O), washed, dried, and weighed. The loss of weight presents the proportion of the fibre which yields to the solvent action of the alkali. (*b*) In a second portion of the fibre boiling is continued for one hour. The loss of weight is an indication of the 'degrading' action of the alkali. In many of the pecto-celluloses the hydrolytic action of the prolonged boiling is such that the non-cellulose is almost completely dissolved away. Generally in this class the loss is considerable, and the difference between the loss in *a* and *b* also. Further, the hydrolytic effect is extended to the undissolved portion or cellulose, and the evidence of the hydrating and gelatinising action is the stiffening of the fibres on drying, and when the action is very pronounced, reagglutination into bundles which dry to wiry strands. This latter effect is minimised by dehydrating the boiled specimen with alcohol and drying at a gentle heat. The hydro-celluloses, as already stated, are not readily attacked by the dilute alkalies, and it is only when digested at very high temperatures that the resolution into cellulose and non-cellulose is effected. In either group it will be found that whatever the condition of the hydrolysis it is always more or less incomplete, and requires, for the isolation of the cellulose, to be supplemented by the treatment about to be described.

"CELLULOSE.—A fresh specimen having been boiled in the dilute alkali (1 per cent. Na_2O), is well washed and exposed for one hour, at the ordinary temperature, to an atmosphere of chlorine gas. It is then removed, washed, and treated with a solution of sodium sulphite, which

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slowly raised to the boil. After two or three minutes' boiling it is washed, on a filter when necessary, though in most cases it may be so placed in a funnel as to act as its own filter, lastly treated with dilute acetic acid, washed, dried, and weighed. The percentage yield on the raw fibre is the most important criterion of its composition and value. We have already pointed out that these celluloses, although similar in external characteristics, are of widely different chemical constitution, and consequently vary considerably in their power of resisting the further action of oxidising and hydrolytic agents. To follow up these cellulosic products into the region of specific variations is a special study in itself, and further investigation must, therefore, be reserved. It is sufficient here to have indicated that the various celluloses are not identical, and that the term is applied to an aggregate of unknown components obtained as the residue from the treatment above described.

"MERCERISING.—The action of concentrated solutions of the alkalies upon the vegetable fibres is an important feature in the diagnosis of their composition. The structural modification which the cotton fibre undergoes under this treatment was originally studied by Mercer, and hence the term 'mercerising,' by which the process is known."

There must of necessity be a considerable variation in the *modus operandi* to suit the peculiarities of the fibre under treatment. A knowledge of this can only come after considerable practice. It will be seen that the figures and recommendations to follow will not in all respects tally with the foregoing. My remarks are intended to apply in a general sense only, and that is all we can hope to do within the scope of this lecture.

From results on a number of fibres tested according to the foregoing scheme, very useful conclusions were arrived at, and this scheme for the analysis and examination of fibres, which was originally worked out by Mr. Cross, was so valued as to be made a general scheme by the Imperial Institute authorities in their researches and publications on industrial fibres, the results of which were published in the IMPERIAL INSTITUTE JOURNAL. With many fibres which I have had occasion to examine since that time I have made use of that scheme of analysis.

I should like to draw your attention to one or two points of interest in connection with the estimation of cellulose. In the ordinary papermaking process for the purification of fibre, an attempt is made to remove all the non-cellulose matter, and to retain only the cellulose as far as is practicable. As a general rule this is done in practice by boiling under pressure with soda, and then washing and finally bleaching by means of calcium hydrochlorite or bleaching powder. In laboratory practice on a small scale, this would entail too much time and too many special appliances. The same result is brought about in laboratory work by boiling in the open with a weak solution of caustic soda for a

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period say up to one hour, so as to soften the fibres and render the lignified or non-cellulose portion of the fibre more reactive to treatment with chlorine. The fibre is then washed to free it from caustic soda, and is loosely suspended in a damp condition in a beaker into which a stream of chlorine gas is passed. If the fibre is a lignified one, that is of the nature of wood or jute, a change takes place, and the fibre alters in colour, but instead of the chlorine having the effect of bleaching the fibre in the way that ordinary bleaching powder does with rags, it combines with the lignin or non-cellulose portion of the fibre, forming what is called a chlorinated product. The fibre is allowed to remain in chlorine gas for about say five hours, at the end of which time there should be excess of chlorine, showing that the fibre has taken up as much as it will. There is a tendency during chlorination for the fibre to rise in temperature, due to the chemical action. This is detrimental, and can be avoided by surrounding the beaker with a jacket of cold water. The chlorinated product is now removed from the beaker and immersed in a dilute solution of cold sulphite of soda. This gives rise to a beautiful red reaction. The red compound so formed is dissolved out on heating the solution after it has been allowed to stand for some time. It will be noticed, therefore, that the non-cellulose has been removed as a chlorinated product, instead of by treatment under pressure with caustic soda, as would be the case in ordinary practice.

When the boiling has been allowed to continue for some time the fibre is washed with hot water, and may be treated with a weak solution of sodium hypochlorite to remove any colour still remaining, then washed perfectly free from bleach and treated with a dilute solution of acetic acid, and again washed; then, in order to get the greatest amount of purification, it can be washed with hot alcohol, and dried off and weighed at a temperature of 105° C.

The bone dry weight of fibre so obtained, calculated on the original bone dry weight, gives a percentage yield of cellulose. The difference between this percentage and the 100 gives us a percentage of foreign matter removed during treatment.

There are many precautions necessary in conducting this treatment. Sometimes it happens that one chlorination is not enough to remove the whole of the lignin. It is a dangerous practice to resort to a second chlorination after boiling with sulphite of soda, although this may be done if care is exercised.

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The best plan in such cases is to use bromine water, by pouring a few drops of bromine into water. The fibre treated with bromine in this way is said to be brominated, that is, a lignified portion combines with bromine and is afterwards treated with sulphite of soda. A soluble compound is produced as with the chlorine compound; the result is the same, but bromine is a much safer substance to use. Instead of sulphite of soda, after the chlorination or bromination, sometimes ammonia is used. This is a very safe chemical for removing the chlorination product, and is a safer one than caustic soda, and far less liable to reduce the yield of cellulose.

I would point out that what is known as the "personal equation" enters very largely into this class of work. A great deal depends upon the exact conditions as to the yield of cellulose obtained.

It is necessary, therefore, to have a good deal of practice at the work.

In regard to the estimation of moisture in the fibre, this is generally done by heating it at a temperature of 105° C.: it is necessary to go above boiling point, because at boiling point some fibres still retain an appreciable amount of moisture. It is necessary here also to exercise a considerable amount of care, because with some products oxidation takes place, oxygen combining with the fibre and actually increasing its weight, besides impairing its qualities.

In other products, on the other hand, there are volatile substances, such as in the case of wood, in addition to moisture, which are driven off at the temperature of boiling water, but for all practical purposes it is near enough if the fibre in question is dried at a temperature of 105° Fahr., and weighed in a weighing tube *until the weight is constant.* The time should not be prolonged beyond this, so as to avoid as far as possible any chance of oxidation taking place.

For more careful work and to avoid the removal of volatile substances other than water, it is best to dry the sample in a desiccator over sulphuric acid. This I have often done and compared with the method above cited, and found to give very good results, although it may take longer and require greater care. The amount of moisture which the fibre is found to contain by the first-mentioned method will give some idea of its purity; the greater the moisture, as a general rule, the greater the impurities; but, in addition to this, the moisture of every fibre is dependent upon the atmospheric conditions. If

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far as possible. As explained before the Dickinson Institute, in order that such results may be of real value, we must take into consideration the weight of a given bulk of wood in our calculations.

Reduction to sawdust should never be used as a means of sampling timber, as in sawdust the ultimate fibres are, more or less, broken asunder, and cellulose so obtained would be no criterion of what we should expect in practice.

Now, I will describe to you the mode which I have made use of for arriving at some more practical knowledge of the way the fibre would behave in ordinary practice:—

Determine percentage of ash by burning 1 gramme until weight of ash is constant. (Note colour of ash.)

Determine moisture by drying at 212° Fahr. until weight is constant; weighing must be done in tube. Determine the cellulose by the following method:—

Boil in dilute alkali until fibre is softened.

Wash, and expose to chlorine gas, for several hours, in beaker, which should be kept cool by surrounding with cold water. (Note whether fibre is changing in colour in chlorine.)

Wash chlorinated fibre to free from HCl, and place in weak solution of neutral sulphite of soda. (Note whether magenta colour is developed.) After one hour boil solution until colouring matter is dissolved.

Wash with hot water.

Bleach with weak solution of sodium-hypochlorite. If cellulose is not white, give further treatment in chlorine gas or in bromine water, but be careful that treatment does not injure fibre. Then repeat treatment with sulphite, wash, bleach, wash, acidify with acetic acid, dry at 212° Fahr., and weigh in weighing tube. The weight calculated on the air-dry original gives the percentage of cellulose.

Note the general appearance and character of the cellulose. Examine cellulose under microscope and note how near it approximates to one or other of the various fibres in common use for papermaking.

From the microscopic characteristics can be judged, in a large measure, the relative value of this cellulose in comparison with other materials.

If sufficient material is available, treat 1,000 grammes in 5,000 grammes caustic soda liquor in a small spherical revolving boiler. The strength of soda must be carefully ascertained by titration at commencement, and care must be taken throughout

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the treatment that no steam is allowed to escape, thus altering the liquor in strength. Boil at 100 lbs. pressure, and draw off at intervals of an hour small samples, which test for free alkali. When the free alkali remains constant discontinue boiling; carefully wash boiled pulp, taking care that no fibre is lost.

Dry and weigh pulp at 220° Fahr.; this weight gives the percentage of unbleached pulp on original weight of fibre. Let the pulp become air-dry by long exposure to air, and until it no longer gains weight; weigh pulp, and calculate percentage of air-dry pulp on raw material; this is the figure that should be taken for commercial purposes.

From the analysis of the liquor you know exactly the percentage of soda neutralised during the boiling. For the purpose of final analysis of liquor, the liquor, together with all the washing, is made up to a known volume, and the "free" and "total" soda are carefully determined. The difference is the soda combined and used up by the fibre.

The original amount of soda added is known. We can easily calculate the weight of soda consumed, and then see what percentage this bears to the original weight of the fibre treated.

We should now conduct another boiling trial, adding soda slightly in excess of that found to be "consumed" in the first trial. The extent to which this soda should be diluted must depend upon the condition of the raw fibre, and must be left to the discretion of the observer. The same pressure is applied (unless there is good reason to suppose that a higher or lower pressure would be advantageous from the general appearance of the first treated lot). Samples are again drawn off every hour, and the boiling continued until no further neutralisation of soda takes place. The rest of the treatment should be conducted as in previous trial. The calculated percentage of pulp should be near that of first trial.

The cellulose should now be determined in a small portion of the bone-dry boiled pulp, and should not be less than 90 per cent.; the ash should also be determined in unbleached pulp.

A portion, say half of one of the boilings, should be carefully weighed and then treated with successive quantities of bleach solution, equal to 5 per cent. of dry bleaching powder at a time. One quantity should exhaust itself before another is added. Any excess of bleach remaining after the colour no longer shows improvement should be determined and deduction from the total added before calculating the bleach consumed by fibre.

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A second bleaching experiment should be done as a check, adding just the equivalent of bleach found to have been consumed in first trial. The bleached pulp is washed, acidified, washed, dried, and weighed, and then exposed to air-dry. Bleached pulp should be calculated upon the original raw fibre boiled. The ash of the bleached pulp should be determined.

Put some of bleached pulp in beater, beat carefully and make into paper on hand-mould, with or without clay, alum, starch, &c.

Take stuff from known mill furnish, and make also into hand sheets, under the same conditions as far as possible.

Compare the relative strengths and other physical qualities. The stuff of known furnish will produce paper on machine of known qualities; from this we can form some rough judgment of what might be expected from the fibre under examination.

Note the comparative shrinkage of the sheets, the comparative felting qualities, and such-like qualities.

From the foregoing work one can form a very fair estimate of value. *Cæteris paribus* the raw material would be in the long run more valuable in proportion as the consumption of chemicals, &c., and treatment was small, the ease with which it can be manipulated, the cleanliness of the pulp, &c., &c. The length of the fibres, the whiteness and purity of the fibre, and also general utility and adaptability are judged from the quality of paper it produces.

It should be ascertained, if possible, how much bulk a given weight of raw fibre will occupy. If bulky, the freight will be high, and possibly preclude its use.

In fibres of low yield and consuming a large amount of chemicals, the cost of chemical treatment per ton of finished stuff is often so high as to condemn the material for industrial use, no matter even if the resulting cellulose is of excellent quality, and the raw material had for the asking.

Such considerations as these must be weighed with the greatest care in estimating the value of of any material for the purposes of paper manufacture.

For the examination of rags I would refer you to my publication in the CHEMICAL NEWS, in which I gave the mode of determining the yield on boiling, and the amount of chemicals used up. If you require to know the loss of any quality of rag that happens to be under treatment in the paper mill, it is a very simple matter to take say 10 lbs. of rags and tie them up in a bag of open material, such as cheese cloth, and throw the same into the boiling of the same rags. When the boiler is discharged

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the bag of rags is fished out, and after washing is carefully air-dried and weighed. The yield can easily be calculated. Many rags contain a lot of dressing. The mineral matter in such dressing can be determined by burning off an average sample, and the total amount of dressing is easily removed by washing in hot water.

As new rags of this description often contain as much as 60 per cent. of dressing, it is a very important matter to determine what the loss is. The most practical way of estimating the value of any particular class of rags is to take a bale of rags and have them sorted and cut into various qualities, weighing each, and as the price of each quality is known in the mill, the value of the original rags can be calculated therefrom.

If time had permitted I should like to have referred you to many other points in connection with this subject, such as the valuation of flax waste, cotton hulls, and other products, but possibly there will be an opportunity of referring to these and other matters in some future lecture.

LITERATURE.—Indian and Colonial Exhibition Reports. (Wm. Clowes & Sons, Ltd. 1887.) Report on Indian Fibres and Fibrous Substances. (E. & F. N. Spon. 1887.) Cellulose. (Cross, Bevan, and Beadle. Longmans, Green, & Co. 1895.) Beadle: PAPER AND PULP, October 15th, 1901. Beadle: The Systematic Treatment of Rags, CHEMICAL NEWS, 1901.

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LECTURE II.

ART PAPERS AS APPLIED TO PROCESS PRINTING.

Art—Imitation art—Nature of surface—Nature of fibres—Minerals used—Preparation and application of coating—Casein—Gelatine—Test for Coating—Preparation of process blocks—Chemical and physical examination—Nature and utility of coated surface.

THE so-called "art" or imitation art papers have come into vogue very much during the last few years.

They have rendered so-called process printing not only possible, but have been largely the means of reducing it to a fine art. Although such papers are by no means artistic, either in appearance or composition, they have through their very nature become the means or medium of rendering art by mechanical processes. It must be remembered that the surface of an enamelled paper is not paper at all. Paper must consist of fibres, and ordinary paper which is not coated partakes not only of the chemical nature of cellulose, but of its physical nature also. The physical structure of the cellulose fibres renders it difficult to impart to paper of any description the fine tones and half-tones of process printing. Any spreading or diffusion of the ink would naturally tend to travel along the tubes of the fibres, but with a coated paper, although there is great power of absorption, there is no tendency to diffuse in one direction more than in any other. On the other hand, when the paper is enamelled, the surface alters its character entirely, and partakes of the nature of whatever mineral matter the enamel contains, the paper itself playing a subordinate part. Assume that the basis of the coating consists largely of clay. In the process of printing the ink does not come in contact with the fibres at all, but merely in contact with the enamelled surface of the paper. In other words, it comes in contact with a uniform smooth surface of clay held together by means of some adhesive material. The ink is absorbed by this surface, and has no tendency to spread, as it might do should it come in contact with the fibres of the paper. But the main difference between the enamelled surface and

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the unenamelled surface of the paper is the degree of smoothness.

Particles of clay are infinitely smaller and finer than the fibres composing the paper, and consequently present a much more uniform and compact surface than fibres would do if uncovered with enamel.

Even with a great deal of glazing with calenders it is impossible to give to the surface of an uncoated paper the same regularity as to the surface of an art paper. If you could very much magnify an art paper when viewed in sections, you would notice the surface of the paper proper, *i.e.*, the waterleaf, has an undulating or wavy appearance, whereas the surface of the enamel, although it might appear granular and show the individual particles of mineral, would present a fairly flat and compact surface.

I will endeavour to give you a brief description of the preparation of the paper, together with preparation and use of the enamel for the manufacture of an art paper:—

An art paper, in order to stand wear and tear, must be made of good material, but if it is not required to be strong, and if it admits of being heavily coated, the fibrous material is not of so much consequence; in fact, I have known common papers heavily loaded with enamel and containing as much as 30 per cent. of mineral matter to consist largely of mechanical wood. The enamelled surface may be made to cover a multitude of sins. When such papers are moistened and rubbed, the whole of the surface, together with the printed matter, comes away, and it can be readily seen, when the enamel is removed, that the paper itself is made of very common material.

Such paper is very deceptive material for any publication which may be required for reference. If exposed to the daylight it discolours and becomes rotten, and easily pulverises. These papers are deceptive because the thickness of the enamel hides their imperfections. When an imitation art paper of this description is used for the purpose of publications, it will be noticed, on turning over the pages, that the paper has quite a leathery feel and sound, although the paper is easily torn. The mineral contained in the enamel will largely influence the character of surface as regards feel and general physical qualities.

Such papers are also very fatiguing to the eye if the printed matter is read in a bright light, especially when the light strikes at certain angles, but they possess in a very high

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degree the power of receiving half-tone impressions, for which they are so admirably adapted. This is their great redeeming feature.

The following is a description of the method employed in the coating of an art paper, as described by "A Reader" in the columns of PAPER AND PULP, January 1st, 1902:—

"The coating machine consists of a cylinder or drum varying from three to four feet in diameter, which acts as a support to the paper as well as a carrier when under the influence of the brushes. The colour box is made of copper, and is arranged so that heat may be applied, in order to keep the colour always at the same temperature. The coating is applied to the paper by means of a vertically-running felt which does not pass through the colour box, but to which the colour is transferred by means of a copper roll running in the box, the amount of coating so transferred being regulated by the degree of pressure of the felt against a parallel roll between which the paper passes. The distribution of the coating is effected by means of five or seven brushes, the bristles being so selected in quality as to become softer and softer in succession. The brushes work with different motions, some being stationary, others moving to and fro sideways, the latter motion being supplied by cranks all fixed on one shaft and driven by belt. At the end of the coating machine is generally fixed a pneumatic suction table on which the now coated paper passes. This table acts as a drawer, and prevents the paper slipping on the drum, after which it passes on to the drying apparatus. This apparatus consists of a system of endless chains, on which are carried sticks, the paper hanging from these sticks in loop form, and is subjected to a temperature varying from 80 degrees to 90 degrees Fahr. If the drying room is not long enough this apparatus is fitted with a turntable, which takes the sticks, describes with them a semi-circle, puts them in turn on to returning chains and finally delivers them into a self-taking and removing apparatus, the coated paper passing on to the reeling machine. After the reel is of sufficient size it is taken off, and in the case of a high class 'art,' is recoated on the opposite side. As a rule, part of the day is devoted to coating one side, and the rest the opposite side. The coating or enamel consists of a mixture of satin white, blanc fixe, enamel or china clay, used in varying proportions according to the desired finish. Gelatine is added to the mixture to size, in order to prevent the coat from lifting when printed. The speed of coating varies according to the width of reel coated, but an average may be taken at 80 to 120 feet, and in some cases at the speed of 140 feet."

Blanc fixe is also known as permanent white, or chemically as barium sulphate. It is prepared artificially, and is much preferred to the natural ground mineral, as the latter is crystallised and has very little covering power or "body."

Satin white is a mixture of hydrated alumina and calcium or barium sulphate.

You will find a good deal of information on this subject on reading through PAPER AND PULP.

The two chief materials used as adhesive materials are gelatine and casein; the latter has come more to the fore of

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recent years, although gelatine appears to possess certain advantages which casein does not. It is difficult to find information on this subject in any of the text-books, but here and there one finds fragmentary references in our scientific literature. For much of the following information, in regard to the use of casein, I am indebted to Messrs. Spicer Brothers, Ltd.

Insoluble casein, as you may know, requires an alkali to dissolve it. The alkalies generally used in practice are either ammonia, soda, or borax. Which alkali should be used, or whether a combination of alkalies should be used, depends upon whether china clay, blanc fixe, satin white, or other material forms the basis of the enamel.

The user must bear in mind that once having got his solution the rest of the work is practically the same as with glue. It may be necessary to neutralise if the blanc fixe or other material is of an acid nature. Some colours used in mills are so acid, that to add the casein solution to them straight away would have resulted in nothing but a curdled mass, impossible to use for coating. When, however, the mixing is neutralised the colours should give no trouble in the working. There are many mills in this country now using the casein, as it gives a clear solution and preserves special features which render it of service for certain work. Casein has to a certain extent been used for engine sizing, particularly in the United States, but not to any extent, so far as I can ascertain, in this country.

For the purpose of making up the enamel the insoluble casein is treated in the following manner :—

As above stated, the casein as received is insoluble, and has been rendered soluble by the addition of either ammonia, borax, or soda.

To every pound of dry casein to be used add three pints of cold water (if very thin coats are required, four pints), and stir the casein in the cold water so that no lumps are left. Soak for ten minutes or so and then apply heat in the usual way, either by turning in live steam or by heating in a steam-jacketed pan. The mass should be stirred while heating, the same as with glue. When the temperature is, say, 100° Fahr. the alkali may be added; and when the temperature has reached 140° or 150° Fahr. the heat should be turned off and the size agitated until a perfectly smooth solution without any sediment is obtained. It is of advantage to dissolve as slowly as possible, as the size will be stronger.

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If ammonia be the alkali used to dissolve the casein, one ounce of ammonia 26 per cent. (or .901 specific gravity) should be sufficient to dissolve each pound of casein used. If the ammonia should have lost any of its strength due to evaporation more will be needed.

For using casein with colours borax is the best alkali to use, as it does not affect the colours nor change the shades. 20 per cent. to 25 per cent. of borax is ample to dissolve the casein, and the borax should be dissolved in part of the water to be used for mixing with the casein.

For white, such as china clay or blanc fixe, the alkali may be monohydrate of soda (Solvay process) or crystal carbonate of soda, the proportion of monohydrate to be used being 12 per cent., and the proportion of crystal carbonate 15 per cent. The soda should be dissolved in a portion of the water used to mix with the casein.

If it is wished to use soda and borax together, take 8 per cent. of either monohydrate or crystal carbonate of soda and 10 per cent. borax; this solvent can be used with clay, blanc fixe, or colours.

For satin white take 15 per cent. of monohydrate of soda or 18 per cent. of crystal carbonate of soda, dissolving whichever is used in some of the water used for mixing the casein.

It must be borne in mind that it is always necessary to have the size on the alkaline side, to get and keep the casein in solution.

There are difficulties to be overcome in regard to the addition of colour both in the use of glue and casein. The following method of testing whether the coating is done in a proper manner is given in the PAPIER ZEITUNG, as abstracted in the JOURNAL OF THE SOCIETY OF CHEMICAL INDUSTRY:—

"For the examination as to the value of the coat there are three tests: (1) The moistened thumb is pressed against the paper and removed. If any of the colour, &c., adheres to the thumb, then the paper is badly coated. (2) A piece of the folded paper is rubbed between the fingers, and notice is taken as to whether any of the coat, and how much, has come off. The most reliable is—(3) A strip of uncoated sized paper covered with the best glue is moistened and pasted on to the coated paper which is to be examined. After drying, an attempt is made to separate the pieces of paper. According to whether the coat of colour adheres to the paste or not, separation takes

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place either along the coated surface or the fibres are torn away. If the former, the coating is bad; if the latter, it is good."

It must be borne in mind that the above test could not be laid down as applying to all coated papers. Some are required to stand better than others. In any case, however, the surface should be such as not to lift on the blocks. The condition of the enamel is largely dependent upon the proportion of adhesive material to mineral matter. Naturally the paper-maker desires to get the proper effect with the least quantity of adhesive. Formaline is often used to render the casein insoluble, so that the coating may be impervious to moisture.

The following particulars in regard to Schmidt's American Patent are interesting in this connection, as given in the JOURNAL OF THE SOCIETY OF CHEMICAL INDUSTRY:—

"When a 5 per cent. solution of soda-casein is mixed with formaldehyde, no coagulation takes place, the solution remains clear and liquid for a long time. But when such a mixture is spread out on glass or paper and allowed to dry, a transparent film of casein is formed which is completely insoluble in water. Films of casein so treated may be distinguished from ordinary films in the following manner. The films are carefully removed from their backings and placed in water to which a couple of drops of methylene blue have been added. On warming, the film which has not been treated with formaldehyde is dyed a pale blue, whilst the formaldehyde film assumes a dark blue colour. A solution of casein in ammonia behaves in a similar manner, but if large quantities of formaldehyde be added, a precipitate is formed. The following proportions are cited: 100 grammes of casein and 1.5 grammes of caustic soda are dissolved in a litre of water, to which are added about 15 grammes of a 40 per cent. solution of formaldehyde, or 100 grammes of casein and 10 c.c. of a 10 per cent. solution of ammonia are dissolved in two litres of water, to which are added about 30 grammes of a 40 per cent. solution of formaldehyde. Either of these gives insoluble films on drying, which may be used for photography, surgical bandages, paper-coating, &c."

In order to appreciate in what way enamelled papers are of service to the printing trade, it is necessary to know something about the various methods for the mechanical reproduction of photographs and process blocks. It is impossible to refer in detail to more than one process. The following description from Mr. J. D. Geddes' Cantor Lectures on "Photography as

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applied to Illustration Printing," recently published in the SOCIETY OF ARTS JOURNAL, gives a very lucid description of the processes involved. This will help you to realise the difficulties with which the papermaker has to contend in the production of paper which will prove itself suitable for the work. It can be readily understood on reading this through that the surface of the paper must be extremely uniform and free from all irregularities. In fact, an ideal art paper should have an absolutely plain surface, so that when viewed under the microscope it should not show any ups and downs at all :—

"PREPARATION OF THE DIAMOND-RULED SCREENS OF MR. MAX LEVY, OF PHILADELPHIA.

"A sheet of the finest plate glass is selected, and is coated with a varnish composed of asphalt and wax. The coated glass is placed on the bed of an automatic ruling machine of extremely accurate construction, and capable of ruling lines of any degree of fineness up to 500 to the inch. The cutter of the machine is diamond-pointed, and gauged to cut lines of any desired width. The lines are ruled diagonally at 45° across the glass, and the number to the inch varies according to the kind of work for which the screen is required. For newspaper printing the lines may be 50 or 60 to the inch; for commercial and catalogue printing, 100 to 130; and for finer magazine or book illustration, 150 to 200 to the inch. When the ruling of the glass is completed, the ruled surface is subjected to the action of the hydrofluoric acid, which eats into or etches the lines laid bare by the diamond, and forms a channel which is filled up with opaque pigment. This enamel is baked in the lines in an oven, and then the surface is carefully polished until the lines are perfectly level and the spaces represented by clear glass are bright and transparent.

"Two of these ruled glasses are required for each screen, laid together with the lines crossing at right angles, and cemented with Canada balsam. As may be imagined, the screen gratings are somewhat expensive: a piece measuring 12 inches by 10 inches of 175 lines costs about £25, whilst large screens of 24 by 18 are charged at £100 or more. I am glad to state that we have now an English firm (Messrs. J. E. Johnson & Co.) who rule these screens excellently, indeed, there is little to choose between this work and the best American, which is a comforting thing to say in these days when it is the habit of the ever-present pessimist to decry everything that is English and all that the Britisher does.

"To produce a half-tone block from a picture, wash drawing, or photograph, this ruled grating is placed in front of the sensitive plate, but not in contact with it. The screen *distance* from the sensitive plate is a point of importance in making the negative, and the skilful operator has to determine this distance according to his experience, and to the character of the subject which is to be photographed. If it is placed too close the resulting negative will present what is known as a gridiron appearance, if it is too far away, the dotting will be too close in the lights and too small in the shadows. You will understand how necessary it is to keep a nice balance in this matter in the case of a picture which is built up entirely of an infinity of dots, shadows being represented by grouping of dots close

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together, with smallest of spaces between middle and light tones by dots of different graduations in size, and the highest lights of pin-point dots only. Everything is represented by dots, yet they are so accurately graded in relation to the light and shade of the original, that the eye does not detect them, unless examined closely, and the half-tone picture appears as a practical fac-simile of the original from which it was photographed.

"The method of printing half-tone negatives on metal is similar in most respects to that described for line blocks on zinc, with this difference. that most half-tone blocks are now etched on copper, and the sensitising solution generally employed for this metal is a compound of fish glue. albumen, chromic acid, water, and bichromate of ammonia. The copper is carefully cleaned with Tripoli powder and washed, the sensitising solution is then flowed over it twice or three times and placed on a revolving table. where it is rapidly whirled in order to spread the coating thinly and evenly over the whole surface; the coating is then dried by gentle heat in a yellow lighted room, and the plate is now ready for exposure. Under the half-tone negative, three to ten minutes' exposure to an electric arc light completes the printing, when the plate is removed to a bath containing cold water, and soaked and washed under a spray of water until the unacted-upon compound is dissolved out, an operation occupying five or six minutes. The imagery on the metal at this stage is almost invisible. In order to enable an examination of the film to be made, the plate is dipped into a solution of methyl violet, which dye immediately stains the film, and brings the picture into view. If all has gone well, the surface is dried either by flowing it with methylated alcohol or gentle heat. The next operation has an important effect, namely, a hardening of the delicate glue picture into a substance resembling enamel, and this gives the method its name—'the enameline process.'

"The plate is simply heated to a high temperature over the flame of a large 'Bunsen' burner. During the progress of this 'burning in' or enamelling, the image changes curiously; the blue picture gets pale, then grey, and eventually vanishes entirely. After a few seconds, as the plate gets hotter, the image appears as a faint brown and gradually increases in strength until it fully attains a rich chestnut brown tint, when the heat must be withdrawn, and the plate is cooled off. The plate has now a picture fixed upon it, which is formed of a strong, hard, impermeable coating of enamel, and which will bear any reasonable amount of etching without further protection. The etching bath is made up of neutral perchloride of iron dissolved in water and of a strength which registers 35 degrees with a Baumè's hydrometer. The plate is first subjected to a general etching all over the plate sufficient to give the block a printing depth, that is, to etch away the spaces round the dots forming the picture so that the plate may be inked over with a printer's roller charged with ink, and a first proof of the photo-etched picture pulled in the press. In most plates made by this process a further and local etching must be performed. The dulling of the general effect caused by the interposition of the necessary screen grating has to be removed as far as possible, and this is done by artists who are specially trained for the work. The parts of the picture which are in shadow and are usually correctly rendered by a properly exposed negative, are covered over with varnish and the next tones are etched again, and these tones are covered up and the high lights are treated until the resulting picture, when proofed, correctly represents the original. The plates are then trimmed by

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engravers, bevelled to admit of being riveted to the wood mounts, and are mounted type-high for use in the printing press."

OTHER PROCESSES, AS DESCRIBED IN "THE STORY OF PHOTOGRAPHY," BY ALFRED T. STORY.

"The best known in England is the Meisenbach process, which, after having been worked by Messrs. Bullock and Swan for a number of years, was patented by Meisenbach in 1882. The process is thus described:—A transparent plate is etched or stippled in parallel lines. A transparent positive is made of the object, the two plates are joined, preferably face to face, and from the combined plates a definite negative is photographed in the ordinary way. In order to cross-hatch and break the lines of the shading, the hatched or stippled plate may be shifted once or twice during the production of the negative. The photographic negative thus obtained may be applied either directly to a zinc plate, or a lithographic transfer may first be made in the usual manner, and the plate subsequently bitten by acid to form a block in relief.

"The Ives process is a very original one in so far as the reproduction of half-tone is concerned, and its excellent results may be seen in many of the American magazines, which until very recently left our English periodicals far in the shade as regards their illustrations. Of late, however, the English magazines have been gaining ground very rapidly.

"In the finer and more artistic forms of photogravure England seems to have been left almost entirely behind—as in so many other departments where exceptional knowledge of technique is required—by the French and the Germans, nearly all the best reproductions of large pictures by photogravure being done at Paris or Berlin."

The following are the results of physical tests on some art papers which I undertook for this lecture. They comprise the following publications: THE GRAPHIC, THE PAPERMAKER, SUPPLEMENT TO THE GRAPHIC, THE SPHERE, BLACK AND WHITE, THE SKETCH, ILLUSTRATED SPORTING AND DRAMATIC NEWS:—

ASHES OF ART PAPERS AFTER THE REMOVAL OF ENAMEL.

No.	Percentage of Ash.
86	22.8
87	16.2
88	19.6
89	15.8
90	22.7
91	29.0
85	19.3

The results as shown in these tables are arrived at by means of a special instrument which I have had made, which, together with the use of a micrometer gauge, has enabled me to work out, not only the weight of a given volume of paper expressed in grammes per c.c., but also the weight of the fi

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The Results of Physical Tests on some Art Papers.

No.	Thickness per 10 discs of 10 square metres area each.	Weight per 10 discs in grammes.	Per cent. Ash by Weight.	Grammes per c.c.			Per cent. by Volume.		
				Total.	Fibre.	Mineral.	Fibre.	Mineral.	Air.
74	.900 mm.	1.100	30.6	1.20	.833	.367	55.5	14.6	29.9
85	.975 mm.	1.260	19.3	1.29	1.040	.250	69.3	10.0	20.7
86	1.05 mm.	1.250	22.5	1.19	.922	.268	61.5	10.7	27.8
87	875 mm.	1.070	16.0	1.22	1.025	.195	68.3	7.8	23.9
88	.975 mm.	1.130	19.5	1.15	.926	.224	61.3	9.0	29.7
89	1.20 mm.	1.370	17.9	1.14	.936	.240	62.4	8.1	29.5
90	1.00 mm.	1.320	22.4	1.32	1.025	.295	68.3	11.9	19.8

No.	Weight per metre Length.	Strip 1 inch wide. Breaking Strain in lbs.				Mean Breaking Strain.			Grammes.	Weight Length in Metres.
		A	A	B	B	A	B	A and B.		
74	2.400	7.0	7.0	11.1	11.1	7.0	11.1	9.05	=4,100	1,710
85	2.890	20.1	13.0	22.0	25.0	11.5	23.5	17.52	=7,950	2,760
86	2.800	12.2	13.0	24.0	25.0	12.6	24.5	18.55	=8,420	3,020
87	2.44	10.4	12.0	14.4	19.0	11.2	17.2	14.20	=6,445	2,650
88	2.58	10 0	11.0	12.1	18.0	10.5	15.0	12.77	=5,780	2,230
89	3.08	10.2	13.0	24.1	25.1	11.6	24.0	18.1	=8,180	2,650
90	2.95	7.0	10.0	18.0	20.0	8.5	19.0	13.75	=6,005	2,040

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ad ash in grammes per c.c. From these results it is possible y a process of calculation, which I have already referred to in my nswer to last year's City and Guilds examination questions, to lculate the actual volume percentages. Thus, if we had, for the ke of argument, a cubic inch of paper, by cutting pieces of a quare inch area and laying them one on top of each other until hey, when pressed down, measured an inch in height, we could ay what proportion of this area was occupied by the cellulose r fibre, what proportion was occupied by the clay, and what roportion by the air space or interstices of the paper. I have ndertaken these few results purposely for use in this lecture. My colleagues and I are engaged in results of this kind in different lasses of paper, on about 90 specimens, with a view of deter-ining whether we can devise some better modes of testing nd classification than is at present in vogue at the Charlottenburg overnment testing station. The results of these investigations vill be published in due course when they are completed.* You vill notice that the air space or interstices of these papers runs rom about 20 to 30 per cent. A shows the breaking strain vhen pulled in the direction of the web, and B when pulled across he web, in lbs. on a one-inch width. This is calculated into grammes, and finally expressed in "weight length," as is done n Germany. The ash of these papers varies from 16 to over 30 er cent., and the heaviest loaded paper shows the least strength nd the least loaded is nearly the strongest. From these tables ou can arrive at useful data, such as the weight per cubic foot, seful for the purposes of stocktaking, and show the relative mount of bulking, useful to printers in arriving at the weight which a given book will require as well as its thickness. The discs re punched out of such a size that the thickness of ten discs in nm. gives the volume in c.c.

As regards the amount of enamel used I should like to point out that this does not bear any direct relation to the weight of paper coated. For a given purpose a certain thickness of enamel would be required. It is a question therefore of area, not of weight. For every ream of demy we might reckon upon an addition to the weight per ream of 10 lbs. If the uncoated paper weighed 20 lbs. to the ream, the coated would weigh 30. If 30 lbs. the coated would weigh 70. The paper is rolled twice and must be rolled sufficiently on the under side to obliterate the wire

* Since this lecture was delivered the results in question have been published in pamphlet form; *see* "An Essay towards Establishing a Normal System of Paper Testing," by Cross, Bevan, Beadle, and Sindall. Wood Pulp, Ltd.

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mark. It should also be coated more heavily on the under si
The coating should be conducted in such a manner as to ensu
absolute evenness and there must be no waviness. When paper
used for chromo-lithography, the enamelled surface should
perfectly neutral to prevent any action upon the colours. Wh
casein is used and it is desired to obtain a neutral coating,
should recommend the use of ammonia as the alkali for render
the casein soluble, and I should consider that this mixture
conjunction with formalin would produce the most water-resista
and insoluble surface.

The difficulty urged against casein is the uncertainty of
behaviour and its liability to give a brittle surface. This m
largely be due to want of skill in its manipulation. The glue
gelatine used as the adhesive material is not that ordinarily us
for the tub-sizing of papers. Tub-sizing gelatine is required of
different nature to gelatine for enamelling purposes, and t
one cannot be used for the other with advantage. The amou
of gelatine (or casein) in relation to the amount of mine
matter as well as the dilution of the paste must be adjusted
suit requirements. This is only arrived at as a matter
experience. If too little gelatine is used the surface will rub
and lift in contact with the blocks; if too much is used the surfa
is of a harsh nature. The enameller desires, of course, to get t
result with the least quantity of gelatine or casein on account
the expense of these products. In course of time the enamell
surface is often acted on by contact with air and moisture a
bacteria, the result being that the adhesive material is destroye
leaving the clay easily removable by rubbing. It is hard
probable that an enamelled paper will last many years, mo
especially in a warm damp climate. For chromo-lithography
absolute freedom from stretch or expansion in contact with the
damp cylinder is an essential quality, otherwise the register will
not be true. Formalin acts not only as a substance to render
the adhesive material insoluble, but is also a preservative. An
art paper, of course, is absolutely useless for writing upon. The
ink diffuses in all directions and soaks through the enamel.
Printer's ink as you know is a mixture of drying oil and pigments.
The printer's block merely imparts to the surface of the enamel
an extremely thin film of ink which is rendered insoluble by
oxidation by contact with the air, but cannot be said to dry in
the ordinary sense of the term. The type and blocks, I believe,
last longer when art papers are used. This I believe to be due to
the enamel wearing the type less than an ordinary sheet of paper

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ɔes. An art paper is extremely opaque, due to the large amount mineral matter it contains. It has a dead or chalky-white ɔpearance. It may be said to bear the same relationship to a ɪeet of pure fibre paper that earthenware does to porcelain. The ɜry translucency of pure paper gives it a superior and refined ɔpearance. Immediately you render a paper dead opaque to light ɔu get a chalky white. In its behaviour towards reflecting light ɪere is this important difference between a glazed sheet of coated, ɪd a glazed sheet of uncoated paper: with a coated paper there only one plane of reflection which is incident with the surface the paper. If a ray of light meets the surface at an angle it is ɜflected *en masse* at the same angle, so that the angle of reflection equal to the angle of incidence as with a mirror. In an uncoated aper, the fibres of which it is composed present to the light ınumerable surfaces disposed at every conceivable angle. When ray of light strikes the surface of such paper, instead of being ɜflected at the same angle it is reflected at innumerable angles ɪd in all directions, giving to the eye the general impression of hiteness and without glare. For reasons above given art papers re most fatiguing to the eye when used for printed matter, and ; is not to be wondered at that so many of the public have raised heir voice against its use for this purpose.

I should mention that the paper used for enamelling, although ɜs composition is not very material, should possess certain pro-erties. It should be rosin sized, but not hard sized. It should ot expand much when wetted by the enamel solution or it is able to buckle. If too hard sized, the enamel would not enetrate sufficiently to keep on. The surface should be free rom dirt and grit or it will give trouble.

What is known as imitation art paper is generally an esparto aper with a considerable amount of mineral in it and perhaps ome wood pulp, and slightly rosin sized, treated by means of the ater doctor. This imparts to the paper what is known as the ater finish. The water doctor is an attachment to the calenders hich holds water and brings the surface of the water in contact ith the surface of the paper just before it enters the nip. Paper an be treated in this way either on one or both sides. The ater added to the paper in this way has to be extracted by the alenders. A double stack of calenders is needed, and a consider-ble amount of heat. One disadvantage of this treatment is to ery materially reduce the bulk of the paper. This process lays own the surface of the paper and flattens the fibres in such a

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way as to produce a somewhat similar effect as enamelling. By squeezing the fibres together it "brings the clay to the surface" and gives the appearance of coating on the surface. With enamelled papers the colour of the paper itself is immaterial—the colouring matter being added to the enamel. Duplex colours can be produced, of course, by means of enamelling. The water doctor can also be made use of for producing duplex colours by placing dyes in the water.

There appears to be some confusion with regard to the name "Art" paper. I take it that the name originally applied to uncoated papers prepared for lithographic work and art illustration. Such papers were, in the first instance, not enamelled at all. The name has got to be applied now to enamelled papers, and the word "art" is now written in inverted commas. What is now known as imitation art paper is paper treated with the water finish.

REFERENCES.—See PAPER AND PULP, December 15th, 1901, and January 1st, 1902: "Manufacture of Art Papers," by a Reader. Read also PAPER AND PULP, May 15th, 1902: Photography as applied to Illustration and Printing. Lecture I., JOURNAL OF SOCIETY OF ARTS, September 19th, 1902. "The Story of Photography," by Alfred T. Story. (George Newnes, Ltd.) See also various articles contributed to the PAPER TRADE REVIEW in 1901 by R. W. Sindall on "Fillers, and their Compositions."

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LECTURE III.

BLEACHING.

Peculiarities of ultimate fibres—Relative lengths—Characteristics—Nature of "chloride of lime"—As powder—In solution—Table of strengths—Effects of heat and time on the storage of bleaching powder—Change of strength on storage of solution—Chlorine gas—Tumbler bleaching—Bleaching in beater—Effects of carbonic acid gas on bleaching solution—The Thompson process — Eau de Javelles — Relative efficiencies of different solutions.

Some of the students have asked me to describe to them the general characteristics of the chief papermaking fibres. These are described in the various text-books on papermaking, but often in a way which is not intelligible to the uninitiated mind. In my lectures before the Dickinson Institute I endeavoured to present a mental picture of the various fibres used in papermaking. I cannot do better than give you extracts from these lectures.

What is needed in order to obtain a mental grasp of any minute object is a model of this object on a large scale, such as has been so successfully accomplished at the South Kensington Museum in the case of the malarial mosquito and the tsetse fly. These insects have been reproduced about eight inches long, every hair and every detail being shown, and giving an impression of being alive.

If we can have models of papermaking fibres on a magnified scale produced in a similar way, we should be able to form a true mental picture of their various characteristics, far better than we are able to do at present by means of the microscope.

*Cotton fibre is a tube with a fairly large hole or canal through the centre, but through the walls being comparatively thin this tube has collapsed, and through collapsing it has assumed a most curious shape, and it is principally this which adds to its value from a papermaker's point of view.

* Dickinson Institute Lecture, October 25th, 1901.

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I shall endeavour to show you how this fibre assumes its corkscrew appearance. If you take an ordinary piece of india-rubber tube, and stop up one end, and then suck the air out of it, you cause that tube to collapse, and I shall endeavour to show you the effect this has upon a piece of tube.

Now, this tube has collapsed, as you see here, and if it is wound round like this, it as near as possible resembles the cotton fibre as we have it in nature: it is really a collapsed tube. The twist is occasioned through the walls being irregular in thickness, as this tube is. This causes it to have a few corkscrew turns in it, even when I do not give it a turn with my hand. A single cotton fibre has anywhere from 15 to 300 twists, counting from end to end.

Now, if it were not for its peculiar corkscrew twists when the fibres interlace one with another, cotton would not bulk paper as it does. Take a number of chair-springs and pack them as close as you can, you cannot prevail upon the wires to go close together, but if you pull the wires out and make them straight they will pack close. We may regard the straight wires as linen, and the springs as cotton, and we have some rough idea of the paper from each.

The cotton fibre is immensely strong, and a single tiny fibre is capable of supporting an enormous weight in comparison with its thickness. You must try and realise that the interlacing of the fibres is like clasping the two hands together; if we clasp hands and pull, we give way because our muscular strength fails: we can't hang on until the bones break.

* Straw and esparto occupy an entirely different position to cotton and linen. The effect produced by any fibre for the purpose of paper manufacture can always be traced to the form, size, and chemical behaviour of the ultimate fibre itself. There is a reason why a particular fibre gives a particular result, and you can trace the result right back to the form of the fibre as seen under the microscope.

Straw is the shortest of the papermaking fibres; you would have to put 75 fibres one on the end of the other to equal the length of one cotton fibre; it is a stumpy fibre as compared with cotton, as it is thick in comparison with its length. Esparto [illegible]ch longer than straw, although much shorter than cotton: straw fibres are quite as thick, whilst others have about the thickness of the cotton fibre.

* Dickinson Institute Lecture, November 1st, 1901.

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I have a table here which I thought perhaps would give you some idea of the relative lengths of fibres. We take cotton and linen fibres as equal to one inch in length. The table further demonstrates that in ordinary beating the cotton fibre is divided into about 30 pieces. The first column of the table shows the number of fibres to the inch, the second column shows the number of fibres necessary if placed side by side to equal an inch in thickness.

I give this table in order that you may be able to form some mental picture of the difference in size, &c., in the fibres as they exist in the paper. You will realise more readily afterwards how these fibres each have their peculiar effect upon the properties of paper.

	No. of fibres per inch lengthwise.	Fibres per inch placed side by side.	Beaten Stuff No. per inch.	Fibres cut during beating into about
Cotton..	1	1,200	30	30 pieces
Linen ..	1	1,200	30	30 „
Straw ..	75	1,250	75	Not cut
Esparto	18	2,200	25	About $\frac{1}{3}$

Straw is so short that it is not cut by the beater knives. Esparto being somewhat longer is occasionally cut, but two out of every three fibres escape the cutting of the knives altogether.

In the case of wood it is a different matter. The wood fibres vary so much in character, some are long and some are short; so you cannot give an average of the length of fibre, or estimate the number of pieces into which the fibres are cut by the action of the beater roll.

Now, in regard to straw, there are certain characteristic vessels by which you can distinguish it from any other paper-making material; they are known as the Parenchyma vessels, and are peculiar oval cells, one on the end of the other. There are also a number of curious serrated cells, which are common to both esparto and straw, and I think you will remember the appearance of these cells best if I tell you they are like the edge of a piece of corrugated iron. The esparto fibre is always recognised by its fine hairs, resembling sharp teeth. If you stroke down a small piece of esparto, as you pass your fingers along you can feel a

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number of small hairs, very fine indeed, millions of them; these help you to distinguish esparto from any other fibres.

That esparto fibre which is really the papermaking fibre has very thick walls and only a small hole through the centre; the ends are solid and rounded, whilst, unlike the cotton fibre, the hole through the centre is so small that it will not allow the tube to collapse. There is something very curious that happens with these fibres when they grow side by side; they are pressing one another very hard, and instead of being round they often get into a peculiar shape—six-sided, like honeycomb. With many fibres this is the case; it is due to the fibres whilst growing pressing one upon the other, and producing a six-sided figure.

The straw fibre is smoother on its surface, and more polished than esparto, and is very much more inclined to take up water; it works wet, and in this respect is somewhat different to esparto in its papermaking qualities, which will be explained presently: this is one of the great distinguishing features between esparto and straw.

When the wood has been chemically treated, the fibres to a large extent lose their characteristics. Sometimes the wood fibre has a number of lattice-work markings on the surface, as in the case of spruce. Spruce is a wood which is used in America, in place of pine, much more extensively than in this country. It is not at all surprising that different kinds of wood yield different qualities of pulp, and produce such a divergence in the qualities of paper; it is only necessary to glance at the various published diagrams to appreciate this fact. By the judicious choice of wood, and also by modifying both the mechanical and chemical treatment it can be made to produce papers, on the one hand resembling a strong linen bank, to soft papers on the other hand which are made to do service in place of esparto. I am told that it can be made to produce good filter paper.

*Many wood fibres resemble cotton, in that they are collapsed or flattened cells, but the cell walls being thinner in comparison with the diameter, the fibre does not present that curious appearance noticeable in cotton. Being consequently more flattened, like an elongated envelope, when seen in section, it does not present the appearance of having the edges turned up to the extent that cotton has. Occasionally the wood fibre is found to be folded on itself, but from its more flattened nature it

* Dickinson Institute Lecture, November 15th, 1901.

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never presents that peculiar corkscrew appearance so characteristic of cotton.

The pine wood has on its surface pitted vessels or pores, generally presenting the appearance of one circle within the other. No two kinds of timber present the same appearance under the microscope, and even the time of year at which the timber has been felled affects the general appearance as well as the dimensions of the isolated fibre. I should like to point this out, as it is not generally known. Taking pinewood, for instance, the fibres that are only one year old are shorter than others that have reached their full growth; when a tree has reached its full development the fibres are much longer.

If you take fibres that are only one year old, you would require 25 fibres lengthwise to make an inch; seventeen years old ten fibres per inch, and fifty years old eight per inch; at fifty years old they have reached their full length. Pine wood yields long soft fibres. Mechanical wood produced from pine, when magnified, gives perhaps the best idea of the general characteristics of wood; the fibres are ranged side by side as in the form of a raft, and generally shows medullary rays in the form of cross markings, and the pitted vessels are most prominent.

With these preliminary remarks on the subject of papermaking fibres, we will proceed to the subject of this evening's lecture.

Before attempting to go into the subject of bleaching from a papermaker's standpoint, we must give some idea of the preparation and chemical nature of *chloride of lime or bleaching powder.

This well-known body was originally considered to be a compound of chlorine and lime. Balard, in 1834, was the first to give an explanation of the constitution of this compound, and his explanation has from that time been generally adopted. According to this view, bleaching powder is a mixture of calcium hypochlorite and calcium chloride $Ca(OCl)_2 + CaCl_2$. Another view of the constitution of bleaching powder has been taken by Odling. He looks upon this substance as a kind of double salt, $Ca \begin{cases} Cl \\ OCl, \end{cases}$ being at the same time a chloride and a hypochlorite.

Chloride of lime is obtained by the action of chlorine gas upon dry slaked lime. When chlorine is passed into milk of

* Roscoe and Schorlemmer, Part 1, Vol. 2, pages 194 and 197.

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lime, a reaction which is analogous to the formation of Eau de Javelle (Vol. 1, page 264) takes place.

$$2\,Ca(OH_2)+2\,Cl_2=CaCl_2+Ca(OCl_2)+2H_2O.$$

If, however, dry slaked lime be employed, a large proportion of the lime remains unaltered. This fact was formerly explained by the supposition that the calcium chloride produced forms a coating round the particles of lime, which prevents the further action of the chlorine. But even if the mixture be from time to time well rubbed down in a mortar, and then again treated with chlorine, it is not possible to obtain a material containing more than 40 per cent. of available chlorine. Hence this substance would appear to be a mixture of basic salt with chloride of calcium, according to the formula.

$$3Ca(OH)_2+2Cl_2=2Ca\left\{\begin{matrix}OH\\OCl\end{matrix}+CaCl_2+2\,H_2O.\right.$$

If water be added to this product the soluble chloride dissolves, and the basic hypochlorite decomposes as follows:—

$$2\,Ca\left\{\begin{matrix}OCl\\OH\end{matrix}\right. = \left\{\begin{matrix}OH\\OH\end{matrix}+Ca\left\{\begin{matrix}OCl.\\OCl.\end{matrix}\right.\right.$$

In practice it is found that 11 cwt. of caustic lime is required to form one ton of bleaching powder. In the preliminary slaking and dressing of the lime probably 1½ cwt. is lost. The lime ready for use contains about 25 per cent. of water, and 1.2 per cent. of carbon dioxide, so that 20 cwt. of bleaching powder would be made up as follows:—

Lime..	9.5 cwt.
Water, 25 per cent. on the 100 of hydrated lime	3.2 ,,
Chlorine, 35 per cent. on the finished B.P. .. say	7.3 ,,
	20.0 cwt. B.P.

*Bleaching powder is made into solution by prolonged agitation or stirring with water. Cast iron is a suitable metal for containing the liquid, steel and wrought iron are acted upon. After the sediment has been allowed to settle, the clear liquid is drawn off, and the sediment or grouts further exhausted by agitation with water. The bleach grouts are thrown away.

It is useful for us to have some ready means of gauging and estimating the strength of our bleach solutions.

Some time ago I constructed a table for the use of paper-makers from the observations made by Lunge and Bachofen, to

* See "The Specific Gravity of Bleach Solutions" (Beadle), CHEMICAL TRADE JOURNAL, No. 323.

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enable those in the mill to determine at a glance the strength of a bleaching powder solution, expressed in pounds of dry bleaching powder per 10 gallons, after merely gauging it with a Twaddle hydrometer.

Degrees Twaddle.	Pounds of bleaching powder per 10 gallons.	Degrees Twaddle.	Pounds of bleaching powder per 10 gallons.
.0	Trace	12.0	10.23
.5	.40	13.0	11.06
1.0	.77	14.0	12.09
2.0	1.59	15.0	13.06
3.0	2.42	16.0	13.99
4.0	3.26	17.0	14.93
5.0	4.14	18.0	15.77
6.0	4.96	19.0	16.66
7.0	5.84	20.0	17.48
8.0	6.79	21.0	18.43
9.0	7.61	22.0	19.43
10.0	8.40	23.0	20.43
11.0	9.34	—	—

Apparently the only basis that papermakers had to go on was the general understanding that a 12° Twaddle solution contained 1 lb. of bleaching powder per gallon.

In order to determine the strength of a solution with the utmost ease and rapidity, it is best to take 10 c.c. and make up to 100 c.c., and titrate 10 c.c. of this with $\frac{N}{10}$ arsenious acid. The number of c.c. used gives lbs. of bleaching powder per 10 gallons without calculation.

Chemists have thoroughly studied the keeping properties of the bleaching powder as sent out by the manufacturers. In cold weather the powder may contain 38 per cent. available chlorine, in very hot weather it may be difficult to produce it to contain more than 35 per cent. The powder deteriorates only slowly if stored in a cool dry place. Heat will cause it to lose its chlorine strength, and, if damp, it will deteriorate either in the hot or cold.

As little is known about the keeping qualities of bleaching powder solutions, I give you the results of my own work:—

The solution taken contained 1.85 per cent. available chlorine, which equals 5.55 per cent. bleaching powder. It

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stood at 7° Twaddle. On the first, second, and third days the solution was found on titration to contain 1.85 per cent. chlorine. On the forty-third day it contained 2.50 per cent. of chlorine, and on the seventy-second day the solution contained 0.202 per cent. chlorine. During the 43 days the solution had *increased 35.1 per cent.* in chlorine strength it originally contained, and during the 72 days the solution had decreased by 89.2 per cent. of the chlorine it originally contained. This apparent anomaly is due to the fact that to begin with, the evaporation of moisture from the surface was far more rapid than the loss of chlorine.

As to the evaporation. During 40 days a similar solution to that taken had lost weight equal to 15.88 per cent., or at the rate of .397 per cent. per diem. During 53 days the solution had lost weight equal to 29.00 per cent., or at the rate of .547 per cent. per diem. For about 50 days the solution underwent very little change in colour, and it appears that up to a certain stage the loss by weight is almost entirely due to the evaporation of water, which considerably increases the percentage strength of available chlorine. That little or no chlorine is given off is evident from the fact that the loss by weight in 43 days is hardly sufficient to account for the increase in the available chlorine found in the solution. After a certain period, which appears to depend somewhat upon the temperature, the solution undergoes a more rapid change in colour, becoming much paler, with a corresponding diminution in chlorine percentage. The more rapid evaporation during the later periods is probably due to the evolution of chlorine or hypochlorous acid, but more probably the former. There appears to be no harm in storing bleach in tanks for six weeks, except in hot weather, the loss of chlorine being almost inappreciable. Beyond this time a rapid deterioration sets in. There is every reason to believe that there is considerable danger in half emptying a store tank or drawing from a tank, the large bulk of which is allowed to remain at the bottom for the most part undisturbed. The undisturbed portion, if allowed to remain too long, may deteriorate and induce rapid deterioration of fresh quantities run into the tank.

Papermakers and other large consumers of bleach who have the bleaching liquor pumped up to a head and distributed by [illegible]tion through mains to the various parts of their works, [illegible]ok into this matter very carefully.

[illegible]above experiments of course apply only to the actual [illegible] under which these trials were conducted. It stands to

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reason that the rate of evaporation of a given bulk, say 100 gallons, would depend upon whether the surface is great or small, and whether the tank is deep or shallow. A covered tank would evaporate less than an uncovered. I should recommend having the tank away from sunlight, covered, and in a cool place, and not too shallow, to prevent deterioration as far as is practicable.

Now that we have got our solution and know something about its chemical properties, let us see what we can suggest in the way of its economical utilisation.* In doing so we will not trouble about recipes and descriptions as given in text-books.

Up to the time of the discovery of bleaching powder chlorine gas was always employed as a bleaching agent. This was obtained by acting on black oxide of manganese with strong hydrochloric acid. At the time that chlorine gas was universally in vogue, rags were the only fibrous material used by the paper-maker. The moist rags, after boiling and washing, were heaped together in an air-tight chamber, into which the chlorine gas was introduced. After the chamber had been filled with the gas, it was left for about 24 hours, until the gas had been exhausted as far as possible and the bleaching completed. This was a troublesome and cumbersome operation, and although effective as far as rag bleaching was concerned, would have been difficult to apply to wood pulp. Chlorine gas has, however, been employed in recent years for bleaching straw pulp, produced by a patented process. The action of chlorine gas, as generally represented, is very simple. It is supposed to take place according to the following equation:—

Cl_2	+	H_2O	=	$2HCl$	+	O
Chlorine		Water		Hydrochloric Acid		Bleaching Oxygen

According to the accepted theory, the oxygen formed oxidises the colouring matter contained in the rags to substances that are colourless. Although chlorine gas is more active and economical in its action than bleaching powder, the latter was very quickly used, on account of its convenience.

The active principle of bleaching powder is a substance called calcium hypochlorite ($Ca(OCl)_2$).

Bleaching powder can be readily dissolved in water to a 10 per cent. solution. For bleaching rags by the aid of this solution the following method has been largely employed. A cast-iron

* This was described at greater length in the following article, now out of print:—"Possible Economies to be Effected in Bleaching" (Beadle), PAPER-MAKER, Special World's Number, 1896.

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receptacle, of the shape of a sulphite digester, known as a tumbler, lined with lead, is filled with rags, and a quantity of dilute bleach solution added. To this is added a small quantity of vitriol. The man-hole door is fastened on and the tumbler made to revolve. This is kept in motion for about 24 hours, and then the liquor is drained off into a tank, and is used again in a new batch. This method of bleaching consumes a large quantity of bleaching agent besides taking a long time. It is necessary that the rags should not be stored for any length of time before being placed in the breaker for washing, as they are liable to become tendered by the presence of the acid. Instead of bleaching the rags, the half-stuff is often bleached in the poacher or in a chest into which the poacher discharges. This takes from 10 to 20 hours, and is often accelerated by the addition of a small quantity of acid. The third method of bleaching rag fibre is to add the bleach to the beater, and to allow the bleaching to take place during the beating of the fibre.

I have carefully compared these three methods of bleaching, and have come to the conclusion that, as regards the amount of chlorine actually consumed, the third method is by far the most economical; but when we come to take into consideration the fact that, in order to get the bleaching done in the time it is necessary to add about twice the amount of bleaching powder actually consumed, and as it is often impossible to use a washing drum on the bleached stuff the unconsumed half of the bleaching powder has to be neutralised by the addition of an antichlor, we find the method is expensive. The following are two sets of tests.

I give you here the conditions of some of the trials in the beater. My conclusions are not based upon one or two solitary trials, but upon a large number of a similar nature:—

(1.) Third quality linens in beater.—224 lbs. dry material, 5.14 lbs. bleaching powder, added in the form of a solution. This equals .802 per cent. of chlorine on dry fibre. Residual liquor after three hours' action contained .0192 per cent. chlorine. As the beater contained 4,560 lbs. of solution, it contained at finish .875 lb. of chlorine, or about $2\frac{1}{2}$ lbs. of bleaching powder unconsumed. Therefore, the amount actually used up in the bleaching was just about half the amount originally added.

(2.) Third quality cotton rags in beater.—224 lbs. dry fibre, bleach liquor added equal to 7.2 lbs. of bleaching powder, which equals 2.52 lbs. of chlorine. This equals 1.12 per cent. of

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chlorine on the weight of dry fibre. The residual liquor after three hours' action was found to contain .020 per cent. of chlorine, which is equal to a total weight of .912 lb. of residual chlorine in the engine, which equals .407 per cent. on dry fibre. In this case, 65 per cent. of the total amount of bleaching powder added was used up in the bleaching.

If it is found necessary to hurry the bleaching more, we must add larger quantities of bleach liquor, and the result is that a larger proportion of bleach is left unconsumed. By comparing these and similar results in the engine with tumbler bleaching, I concluded that, for the actual amount of chlorine consumed, bleaching in the beater was much more economical, but on account of the necessity of adding a chemical to neutralise the free chlorine remaining the total cost was greater. The reasons that the actual amount of chlorine consumed in the beater is so much less appear to me to be as follows:—Firstly, the rags are to a large extent cleansed of dirt when washed in the breaker. This dirt would consume some of the bleach. Secondly, the rapid agitation of the beater-roll accelerates the action of the bleach. It is always found more economical to agitate during the bleaching. Thirdly, apart from the actual agitation, the beater-roll aërates the stuff and brings it also in contact with the carbonic acid of the atmosphere. The carbonic acid helps to set free hypochlorous acid, which is more active and economical in its action than when combined, as calcium hypochlorite. The change takes place according to the following equation.

$Ca(ClO)_2$	$+ CO_2 =$	$CaCO_3$	$+ 2HClO$
Bleaching Powder	Carbon Dioxide	Chalk	Hypochlorous Acid

As, however, the atmosphere only contains about four parts of carbonic gas per 10,000, the action is comparatively slow. The application of carbonic acid in connection with bleaching powder solution was patented in 1855 by P. F. Didot, and in 1883 Thomson patented a process in which he used carbonic acid to accelerate the action of the bleaching powder solution for the bleaching of fabrics. This, however, was never used successfully, as far as I am aware, for the bleaching of rag stuff. It consisted in exposing the cloth under treatment alternately to the action of the bleaching powder solution and carbonic acid gas. I have seen Thomson's process applied to rags in a closed chamber by damping rags with weak bleach, placing same into chamber, and passing in CO_2. If the CO_2 had been introduced as a slow stream

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in front of beater-roll, the process, in my opinion, would have stood a good chance of success. In practice the difficulty which presents itself is the production of CO_2. This might be accomplished either by using a carboniser such as is used in Archbutt and Deeley's water-softening plant, or when practicable the furnace gases might be employed. Both gases might need to be washed through water to remove any sulphurous acid, which if allowed to remain would act as an antichlor.

In order to accelerate the action of bleaching powder solution, I have passed carbonic acid through a 2 per cent. solution until the lime was thrown down. I have found this far more rapid in bleaching effect than ordinary bleach solution. A single experiment will demonstrate this.

Ordinary bleaching powder solution of the above strength turns a red litmus paper blue on account of the free lime that it contains, at the same time it only slowly bleaches the litmus. On passing through carbonic acid the solution becomes milky through the formation of carbonate of lime. This turns blue litmus paper red on account of the presence of free hypochlorous acid in solution; in addition to this the paper is rapidly bleached. The equation is as follows:—

$$Ca(ClO)_2 + CO_2 = CaCO_3 + 2HClO.$$

If, however, the carbonic acid is added in sufficient quantities to re-dissolve the lime, we have a solution containing bicarbonate of lime and hypochlorous acid together. This gives an acid reaction with litmus, and for some purposes is a safer solution to use for bleaching than the one previously described, and for the following reason. The milky precipitate formed, when only sufficient carbonic acid is added to precipitate all the lime, if allowed to settle, as is the case when the liquid is stored in a tank, leaves a solution containing nothing but hypochlorous acid. When this is used for bleaching, free hydrochloric acid is formed, which by some process or other must be neutralised—

HClO	=	HCl	+	O
Hypochlorous Acid		Hydrochloric Acid		Bleaching Oxygen

When sufficient carbonic acid is used to redissolve the chalk precipitate, we obtain bicarbonate of lime in solution, which will prevent the formation of hydrochloric acid by the formation of calcium chloride—

$$CaCO_3CO_2 + 2HClO = CaCl_2 + H_2O + 2CO_2 + O$$

This solution has the advantages of ordinary bleaching powder, without its disadvantages. It is extremely active and economical,

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whereas bleaching powder is sluggish and wasteful in its action. Furthermore, it has the advantage over free hypochlorous acid, in that there is no formation of free hydrochloric acid after bleaching.

I do not think that it is generally known that so much depends upon how the hypochlorites are made and used. There is room for immense improvements and very substantial economies, if the knowledge which we now possess is followed up and taken advantage of.

Until the discovery of Hermite's solution, it was generally supposed that 1 lb. of chlorine would do a definite amount of bleaching. This, however, was disproved when Hermite's solution was compared with bleaching powder. Hermite's bleaching solution is produced by electrolising a dilute solution of magnesium chloride, and in his later patent by electrolising a mixture of common salt and magnesium chloride. The bleaching substance formed is magnesium hypochlorite, $Mg(ClO)_2$. On taking two solutions, one of bleaching powder and the other produced by Hermite's process, containing equal amounts of chlorine, the latter was found to bleach wood pulp much more rapidly than the former, and when the action was complete, for every 5 lbs. of chlorine consumed in the former solution, only 3 lbs. were consumed in the latter. These claims were fully set forth by the inventor, and have been verified by Messrs. Cross & Bevan, Professor Pictet, and myself. Cross & Bevan and Pictet made their determinations upon wood. I made a series of experiments in the beater with different qualities of rags. In each case I found the relative efficiencies to be, as near as possible, as above stated—namely, as 3 is to 5. It is not yet known why the chlorine in the two solutions acts differently, but I shall endeavour to give an explanation or a theory that may possibly account for it in my next lecture.

Before the discovery of bleaching powder by Tennant in 1798, Berthollet found that chlorine could be absorbed by a solution of caustic potash, and the solution possessed the same bleaching properties as the gas. This solution is known to this day as Eau de Javelles. It was extensively used on the Continent for bleaching purposes. The active principle of this solution is potassium hypochlorite. It is, however, too expensive to compete with bleaching powder. A solution somewhat similar in properties to this can be prepared by adding sodium carbonate solution to a solution of bleaching powder. The

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active principle in this is sodium hypochlorite. It is formed according to the following equation:—

$$Ca(ClO)_2 + Na_2CO_3 = CaCO_3 + 2NaClO.$$

Bleaching powder and carbonate of soda gives chalk and sodium hypochlorite. The chalk formed is allowed to settle out. This solution is used in some mills in place of bleaching powder solution. It offers certain advantages which will be pointed out hereafter. Some works, instead of buying bleaching powder and converting it into a solution, generate chlorine gas, which is bubbled through a solution of milk of lime.

By this last-mentioned process calcium hypochlorite is formed. But this solution, although generally considered chemically identical with that obtained from bleaching powder, is very different in bleaching effect. It is generally known that these solutions behave differently from each other as regards their rate of bleaching, and it is supposed that hypochlorite is much more sluggish in its action than bleaching powder solution.

In order to see which form of bleaching liquor was most economical I prepared three solutions as follows:—

(*a*) A solution prepared by passing chlorine gas through milk of lime.

(*b*) A solution of ordinary bleaching powder.

(*c*) A solution of sodium hypochlorite, prepared by adding carbonate of soda to bleaching powder solution, as previously described.

The available chlorine of each of these solutions was carefully determined, and water was added to each in sufficient quantity to make the strength equal to exactly 5 grammes of chlorine per litre. I took 5 grammes of unbleached wood pulp and mixed it with 200 c.c. of water, and after thoroughly pumping I added 200 c.c. of solution *a*. By the side of this I treated solutions *b* and *c* in a similar manner.

After 19 hours' action the wood, in each case, was bleached. I withdrew equal quantities of solution from each, and determined the amount of chlorine. As each solution was diluted with its own volume of water, the solution in contact with the pulp was equal at the start to $2\frac{1}{2}$ grammes per litre of chlorine.

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After the bleaching the chlorine determinations were as follows :—

	In Solution.	Consumed.
(*a*)	1.777 per cent.	.725 per cent.
(*b*)	1.296 ,,	1.204 ,,
(*c*)	1.757 ,,	.743 ,,

It will be seen from the above that bleaching powder solution is the least economical of the three. Supposing that with bleaching powder, in order to bleach a certain weight of wood pulp we consume 100 lbs. weight of chlorine for a milk of lime solution. Saturated with chlorine gas we should require only 60 lbs. weight of chlorine, added in the form of a solution of sodium hypochlorite. It will be seen, therefore, that it is not fair to base the value of a bleaching solution merely on the amount of available chlorine that it contains. It is necessary, in addition to this, to determine what amount of bleaching work the chlorine is capable of doing. It appears that the bleaching effect of chlorine depends largely upon the state of its combination. Why this is so nobody, so far, has been able to discover. It has generally been supposed that, as previously explained, the chlorine acts upon water, decomposing it, forming hydrochloric acid and liberating oxygen, and that the oxygen is really the bleaching agent. Ordinary oxygen, such as the greater part of the oxygen contained in the atmosphere, is incapable of bleaching, but ozone, which is obtained by electrifying ordinary oxygen, is a powerful bleaching agent.

If the above theory of bleaching is correct, it may be that the oxygen formed during the bleaching is only in part active. The efficiency then of a bleaching solution would depend upon the proportion of active oxygen formed during the reaction.

A recent investigator has, however, come to the conclusion that bleaching is not dependent upon the formation of oxygen in the case of the hypochlorites. He dissolved hypochlorites in a medium containing no oxygen, and added coloured substances, which he found to be bleached. He came to the conclusion that some of the hydrogen of the substance to be bleached was seized upon by the chlorine, forming hydrochloric acid, and that bleaching was really a process of reduction and not of oxidation. This, however, has by no means been proved in the case of ordinary solutions; and I do not think there is sufficien reason to warrant us altering our views on the subject. W next have to consider why it is that one solution bleaches s much more rapidly than another. This appears to be closely

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connected with the work that the chlorine will do. As a rule, when the chlorine acts rapidly, the amount required to bring the colour up is comparatively small. This has been explained as follows:—That bleaching is effected by a bombardment of the atoms of oxygen. If the bombardment is active, the atoms which compose the molecules of the colouring matter are, as it were, kept in motion. If the bombardment is slow, the atoms are able to return to a state of rest, and before they can be set in motion again a good deal of work has to be expended by the oxygen molecules to overcome their inertia. This is a somewhat elaborate theory. It will perhaps be better understood by the following illustration:—By the old method of "pile-driving" a heavy weight is lifted to a certain height and allowed to drop. Every time the weight falls the pile is driven a small distance into the ground. By the more modern system a machine is used, which in action is something like a steam hammer dealing a succession of rapid blows upon the head of the pile. By the old method a good deal of work is expended in overcoming the inertia, whereas by the latter process the pile is never allowed to come to rest. It is claimed that the economy of the steam piledriver is due to the fact that the pile is always kept in motion. It is possible that a bleaching solution that is rapid in its action is economical also for a similar reason. It is possible, however, that ordinary bleaching powder solution is wasteful, on account of the chlorine being given off into the atmosphere.

Solution *a* during the bleaching did not smell of chlorine, whereas solution *b* had a strong smell of chlorine, but *c* had only a very slight smell. But setting aside all theories, I think that my results, and those of other investigators, are sufficient to show that chlorine as a bleaching agent varies very much according to the state of its combination, and I hope that this will cause others, who have better opportunities than I have, to study the subject much more closely.

In my next lecture we will go further into this interesting subject. I have left you purposely in doubt on one or two points; I hope to give you an explanation, which I believe to be a true one, as to the cause of these differences in "bleaching efficiencies," but the extent of the subject renders it impossible for me to cover the ground in one lecture.

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LECTURE IV.

THE CHEMISTRY OF BLEACHING.

Early history of bleaching—Sun bleaching—Ozone—The atmosphere—Its bleaching effect—Sunlight—Hermite electrolytic bleaching—"Still"—"Circulating"—Continuous use of bleach liquor—Temperature of bleach liquor.

*It appears that the Egyptians and the Phœnicians during the early ages were well skilled in the art of bleaching. It is stated in the ENCYCLOPÆDIA BRITANNICA that down to the middle of the eighteenth century the Dutch possessed almost a monopoly of the bleaching trade, although mention is found of bleach works at Southwark, near London, as early as the middle of the seventeenth century. It was customary to send all the brown linen, then largely manufactured in Scotland, to Holland to be bleached. It was sent away in the month of March and not returned till the end of October, being thus out of the hands of the merchant for more than half a year.

The Dutch mode of bleaching, which was mostly conducted in the neighbourhood of Haarlem, was to steep the linen first in a waste lye, and then for about a week in a potash lye, poured over it boiling hot. The cloth, being taken out of this and washed, was next put into wooden vessels containing buttermilk, in which it lay under a pressure for five or six days. After this it was spread upon grass, and kept wet for several months, exposed to the sunshine of the summer.

Since that time these processes have gone through a number of evolutionary changes. A boil in carbonate of soda has taken the place of the above-mentioned alkaline treatment, which was known as "bucking." A soak in dilute muriatic acid has taken the place of treatment with buttermilk, and a treatment with a weak solution of bleaching powder, called the "chemick,"

* The first portion of this Lecture is largely abstracted from an article originally contributed to the PAPER-MAKER, but now out of print: "Bleaching: The Primitive Methods of our Fore-fathers" (Beadle), September, 1895.

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has superseded wetting and exposure for a long period to the sun's rays, the latter of which was known as "crofting." The most recent development is the Mather Patent Open Bleach System, by which the cloth is bleached on large open rolls from grey to white without unwinding in 14 hours. Although the above historical facts appear to have little bearing on the bleaching of paper-stock, a knowledge of the chemical action that takes place in these primitive methods of bleaching will, I believe, throw light upon the whole question of bleaching, and assist us in clearing up certain anomalies that appear to exist in the behaviour of solutions of different hypochlorites when used for bleaching.

This primitive bleaching—in which the sun's rays were called into requisition—was, and still is, generally known to this day as sun bleaching. It is quite natural that, during the early ages, the sun should be made available for this purpose, as by repeated washing and hanging out to dry in the sun of any unbleached fabric, the same is found to be very much whitened. The chemical changes that take place in sun bleaching, like a large number of other chemical changes, can only be wrought in presence of moisture. There are only certain of the sun's rays that are able to assist the bleaching. These are known as actinic rays, and are those rays that are able to promote chemical action. The action of the sun's rays upon the atmosphere through which it shines is to produce two substances which have strong bleaching properties. These two substances are ozone and hydrogen peroxide. Ozone is a condensed form of oxygen, and is being continually formed from the oxygen ever present in our atmosphere. A molecule of oxygen is represented as O_2, and a molecule of ozone as O_3.

Ozone is formed from oxygen as follows:—

$$3O_2 = 2O_3.$$

Three molecules of oxygen become two molecules of ozone.

Now ozone is a much less stable body than oxygen, and its molecules being in a state of unstable equilibrium, as it were, it requires very little toppling over to its much more stable condition of molecular oxygen. When a coloured substance, such as unbleached cloth, comes in contact with ozone in the atmosphere, this toppling over is effected, and the ozone is transformed back to oxygen. Ordinary oxygen (molecules of oxygen) is unable to bleach; but what is known as "nascent" oxygen—that is, oxygen just freed from its combination and in its free

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state—is able to bleach. Ozone, by breaking down to ordinary oxygen, provides a source of nascent oxygen.

$$O_3 = O_2 + O$$

Ozone becomes ordinary oxygen and nascent oxygen.

Hydrogen peroxide, the other bleaching constituent of our atmosphere, is also an unstable compound, and this, in contact with substance capable of being bleached, liberates nascent oxygen and forms water.

$$H_2O_2 = H_2O + O$$

Hydrogen peroxide = water and nascent oxygen.

Hydrogen peroxide and ozone are often formed simultaneously. It was generally believed that ozone was formed by electrical discharges in the atmosphere, but it has been proved that it is invariably formed when water evaporates, and it is to the latter source we would rather look for the ozone that takes an active part in the bleaching of cellulose. Both the above bleaching agents may be expended uselessly when brought in contact with substances to be bleached. Ozone is, however, reduced to ordinary oxygen when in contact with some organic substances. When it is expended usefully, only one-third of the ozone can oxidise the organic colouring matter, the other two-thirds going to form ordinary oxygen.

$$O_3 = O_2 + O$$

Ozone = ordinary oxygen and nascent oxygen.

When it is expended uselessly by reduction in contact with organic matter the equation is:—

$$2O_3 = 3O_2$$

Hydrogen peroxide, when bleaching, liberates one atom of nascent oxygen with the formation of water.

$$H_2O_2 = H_2O + O$$

The economy and rapidity of the bleaching depends upon the prevention of the reduction of ozone to ordinary oxygen, and of hydrogen peroxide to water and ordinary oxygen. In short, it is necessary to ensure that the conditions are such that the liberated nascent oxygen is made to enter into combination with the organic colouring matter, with the formation of colourless oxidised products, instead of being reduced to ordinary oxygen.

Ozone is generally supposed to be more abundant during sunshine, and that the absence of the sun's rays allows of the reduction of ozone to ordinary oxygen, especially in the vicinity of crowded cities, where the issuing organic gases to a large extent assist the reduction of ozone to ordinary oxygen. The

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heat rays emanating from the sun may bring about the formation of ozone by the evaporation of water, which is supposed by meteorologists and chemists to be the chief source of ozone in the atmosphere. The actinic rays from the sun may change the molecules of ordinary oxygen into ozone, but this, as far as I am aware, has never been proved. There can be little doubt, however, that the actinic rays from the sun are such as to render the colouring matter of fibres susceptible of attack by nascent oxygen, ozone, or hydrogen peroxide. When a cellulose material, such as unbleached rags, is spread out upon grass and exposed to the sun's rays during summer, it will be found that the material is gradually bleached: it will be found also that the bleaching is very much accelerated by periodical damping with water. We must assume, first of all, that hydrogen peroxide and ozone are present in an open space where the sun is shining, and that the evaporation of water used to damp the material gives rise to the formation of further quantities of ozone. The water also being a solvent for both hydrogen peroxide and ozone, the oxidising agents are brought into immediate contact with the material. The production of ozone is promoted by alternations of damp and dry and hot and cold air. The hoar frosts and morning dews also increase the hydroscopic moisture of the cellulose, besides supplying a quantity of surplus moisture which is evaporated on exposure to the sun's rays. Sun bleaching was never studied at all in a scientific manner, as the use of bleaching powder came in long before the chemistry of sun bleaching began to be understood. To appreciate how precarious this process is, it is necessary to have some knowledge of the intensity of the sun's rays at different hours of the day and at different seasons of the year. When the sun is perfectly perpendicular, as in equatorial regions, the amount of light intercepted by the atmosphere on a cloudless day amounts to 16 per cent. of the total. When the sun is at an angle of 30 degrees with the horizon it has to shine through the depth of two atmospheres, and only 70 per cent. of the total light reaches the earth. When the angle is 20 degrees only about 60 per cent. reaches the earth. When at an angle of 8 degrees only one-fifth the total rays reach the earth; and when the sun is about to set only 2 per cent. of the rays reach the earth. We see then from this that the bleaching power of the sun's rays is greatly diminished as it nears the horizon, and as the sun is nearly always at a considerable ngle, we get very far short of the maximum effect of the sun's ays. Another point in this connection is worthy of notice.

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The rays intercepted by the atmosphere are just those that are most active in their bleaching effect, namely, the actinic rays. The other rays are inoperative in so far as they do not affect the colouring matter to be bleached. The heat rays may promote the evaporation of water and so manufacture ozone, but their function is probably small in comparison with the actinic rays. At any period during daylight some actinic rays reach the earth, but these diminish much more rapidly with the angularity of the sun than do the total rays that reach us. To these ever-changing conditions must be added the uncertainty of the weather, which makes sun bleaching more uncertain even than harvesting. It appears that grass or sun bleaching is less destructive than hypochlorite bleaching, and on this account it is still made use of to a limited extent in the textile trade, and, I believe, has been seriously considered recently as a means of bleaching rags for papermaking.

In some old text-books on papermaking I have seen it stated that the bleach-house should be constructed with as much glass roofing as possible, so that the bleaching operations should be assisted by the sun's rays. As hypochlorite bleaching is so much more rapid than sun bleaching, the latter can be of very little service in conjunction with the former. The old method of rendering raw material white before the introduction of the modern methods of boiling and bleaching may be of interest and throw some light on the subject. This is my only reason for describing these obsolete methods. In ancient days the sorted rags were well wetted with water and heaped up for several weeks until they got thoroughly warmed in the centre. They were occasionally turned to prevent superheating and, consequently, spontaneous combustion, which might subsequently ensue. By means of the above process the non-cellulose, which included resinous matter, oily matter, organic dirt, &c., was more readily oxidised than the cellulose, and consequently converted into soluble products that could be readily removed by subsequent washing. There is much danger of tendering the fibre by conversion into oxycellulose, and in the presence of nitrogenous substances such as gelatine this change appears to be much more rapid. Even with fairly pure fibre a mould is very readily formed. With bleached half-stuff that has been allowed to remain in large lumps for a time in a cool, damp place, a black mould is often developed, which, if allowed to spread, does considerable destruction to the cellulose.

After the rags had been submitted to the above process,

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which took the place of our modern process of boiling with alkali under pressure, they were, after thorough washing to remove the soluble products, spread out on grass in the sun and occasionally damped with water until they were thought to be sufficiently bleached for what then took the place of our hollander. The beating operation was generally done in a large mortar, into which a large pestle was made to drop by means of a crank. The treatment that the rags here received was equivalent to what might be got by stamping rags to pieces in water with an ordinary pestle and mortar.

As far as I know, there was no washing process during the disintegration of the fibre. The cleansing of the material depended entirely upon the heaping up or tendering process and the sun bleaching and their attendant washings. It appears that a large portion of the cellulose was not affected by the tendering process, although the fabric came to pieces more readily. The papers made before the introduction of chemicals have stood wonderfully well, and whatever objections may be raised against these primitive processes, the net result was good, and it appears that the rags were purified and converted into paper with a minimum effect upon the cellulose itself. It appears, at any rate, that the cellulose finding its way into the finished paper was remarkably inert to atmospheric influences. This is undoubtedly largely due to the fact that the papers were free from the residue of chemicals which is to be found in all papers the fibres of which have been submitted to chemical treatment. These methods had been greatly improved if they had been studied in a scientific manner by papermakers. In the light of our present knowledge, great advances might yet be made in this direction. The great objection to these processes is the time required. They took as many months as our present methods do hours. With a warm solution of a hypochlorite and a gentle circulation of the liquor, as much bleaching can be effected in one hour as is possible in one month in summer with a good sun. With the discovery of chlorine and its bleaching power, and the subsequent discovery of calcium hypochlorite or bleaching powder as a bleaching agent, sun bleaching was rapidly abandoned. The chemistry of sun bleaching is very closely allied to the chemistry of hypochlorite bleaching: the active principle is the same. I have given a general outline of these antiquated and obsolete methods not because they are likely to be of any particular value in themselves, but because I feel that some knowledge of them is necessary in preparation of what is to follow.

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We referred briefly in our last lecture to the Hermite bleaching solution, got by electrolysing a solution of magnesium chloride.

As far as I am aware there are no published results of experiments upon the bleaching efficiency of the Hermite bleaching solution in comparison with that of a solution of bleaching powder upon the bleaching of cotton and linen fibre. All the published results, viz., those of Messrs. Cross & Bevan and Professor Pictet, are, I believe, upon the bleaching of wood pulp.

I have made a series of experiments to determine whether the Hermite solution still gave the same efficiency when used for bleaching cotton and linen rags and rag half-stuff. These results were published in the CHEMICAL NEWS. For the purpose of these trials a small beater was used, similar in construction to the paper-maker's hollander.

I took half-stuff produced from second quality linen rags and from second quality cotton rags. Before doing experiments in the small beater, I mixed a known weight of each of the half-stuffs with a carefully ascertained volume of Hermite solution, also with bleaching-powder solution, the chlorine strength of each having been carefully ascertained.

The time required to bleach the materials to a full white was noted, and when the bleaching was complete the available chlorine in the residual liquors was determined, and the amount of chlorine consumed by the fibre calculated.

The following are the results:—

Half Stuff.	Put in		Strength per Litre Grms.	Per cent. on Fibre.
	Dry Weight. Grms.	Liquor.		
1. Linen	162.6	Hermite	3.8	17.2
2. „	162.6	Bleaching Powder	3.16	19.4
3. Cotton	176.2	Hermite	2.8	15.9
4. „	176.2	Bleaching Powder	3.16	18.0

Consumed:—

	Chlorine. Grammes.	Chlorine per cent. on fibre.	Time of bleaching.
1	2.44	1.5	30 minutes.
2	3.72	2.29	4 hours.
3	4.0	2.27	2 „
4	6.49	3.68	10 „

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The efficiency of chlorine in the Hermite liquid as compared with that of chlorine in ordinary bleaching powder is claimed by the inventors to be as 5 is to 3. This has been substantiated by the results of Messrs. Cross & Bevan and Professor Pictet.

3 : 5 : : 1 : 1.66

Comparing this with the experiments above—

	Hermite.	Bleaching Powder.
1 and 2	1.5	: 2.35 : : 1 : 1.54
3 and 4	2.27	: 3.68 : : 1 : 1.65

These results, therefore, confirm fairly closely those of other observers. The next two experiments were done with a view of finding how long the Hermite solution took to exhaust itself if the chlorine put in was the exact amount necessary, according to the above experiments, to do the bleaching.

The rate of bleaching was much slower than if the chlorine had been used greatly in excess. After three days, however, the liquid only contained the least possible trace of chlorine, and the fibre appeared to be perfectly bleached.

The preceding experiments were all done with "still" liquor. In the following experiments the half-stuff was put into the small beater and the Hermite liquor allowed to flow round the beater, and was washed out again by means of a washing drum, from whence it was delivered to a store tank and then again to the beater. The total amount of liquor was first of all measured both into the beater and into the store tank, from which a sample was taken and tested for chlorine. This experiment was not done under the most favourable circumstances, as the liquor was drawn from the store tank and not from the electrolysing tank whilst the electrolysis was going on, which I think would have made a considerable difference to the results.

Put in :—

Half-Stuff.	Weight Dry Fibre. Grms.	Volume of Liquid.	Strength per Litre. Grms.	Per Cent. on Fibre.
Linen . . .	542	56–12	2.64	27.3
Cotton . . .	470	56–12	2.64	31.5

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Consumed :—

Weight of Chlorine.	Per Cent. on Fibre.	Time.
5.6	1.03	40 minutes.
5.6	1.20	60 „

It is evident that the circulating liquor is more economical than the non-circulating.

Half-Stuff.	Non-circulating Chlorine Consumed.	Circulating Chlorine Consumed.	Saving by Circulating over Non-circulating.
Linen ..	1.5	1.03	30 per cent.
Cotton ..	2.27	1.20	47 „

My results confirm those of other observers as regards the rapidity of bleaching by the Hermite solution, which I found to bleach very rapidly, doing as much work in thirty minutes as bleaching powder solution of the same strength would do in three hours.

I also found that Hermite solution will bleach in one treatment: in some instances where any amount of bleaching powder will fail to do so without an intermediate acid treatment. The solution can be used either circulating or stored in tanks for use like ordinary bleaching powder solution, but the latter, as we have seen, does not give such good results.

If it were not for practical difficulties in regard to the production of the electrolysed solution, the Hermite liquor might have proved a great success. It was never successfully installed in any mill in this country, although it was in operation in France. The necessity of having to return the liquor from the potcher to the electrolysing tank to be revivified went very much against it. If any electrolysed solution is to become a practical success it must be of such a nature that weak solutions can be completely and economically electrolysed, so that when the bleaching is accomplished the spent liquor can be thrown away without loss. This neither the Hermite nor the Andrioli solutions were able to fulfil.

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After having gone into the theoretical aspect of the chemistry of bleaching, we will now go to consider the more practical details.

Boiled rags were formerly bleached in the old-fashioned tumblers, but for many years now some mills have bleached the rags by piling them up in chambers and promoting the circulation of warm bleach through the mass, much on the same principle as that of a vomiting boiler, but taking care that the temperature does not rise above 95° Fahr. The rags are not disturbed during the treatment, but the liquor is in constant circulation through the mass, and the action is very rapid and produces a very good colour. The liquor is immediately drained off. If the rags are at once transferred to the beaters after douching them with cold water there is no fear of injury, but if left piled up in a warm condition the centre of the mass undergoes a most curious change. On turning the mass over for its removal to the beaters after, say, a fortnight, or even after a few days, we notice a sweet beeswax-like smell. Whilst the rags are being broken in, if you look along the surface of the water after it leaves the back fall, a thin film is often noticed. If much of these rags is used in the breaker the surface of the latter is soon coated with a thin wax-like film, which can easily be scraped off. This film has been submitted to careful examination. It may become a source of constant annoyance by breaking off and finding its way into the paper. Under these conditions of hot bleaching, instead of the bleach converting the cellulose into oxycellulose, it undergoes a fatty degeneration by slow conversion into a waxy substance, which, by treatment with alkali, is easily saponified and converted into a soap. This action occasionally occurs, giving rise to the so-called waxes and rosins, and is certainly a drawback to this form of hot bleaching, and may result also when stuff is bleached hot in the bleacher and allowed to drain without cooling.

The advantages of the above method are its great rapidity as compared with cold bleach; it is performed with a minimum quantity of liquor, so that the chlorine can be used at its maximum strength; it can be applied to the rags without their being tumbled about. It is somewhat difficult to ensure even penetration. The method, I believe, has been in vogue for many years, but it is difficult to maintain a uniform temperature without careful attention.

The liquid which drains away from rag-bleaching should, in my opinion, not be used again on another batch, as it acts upon and tends to exhaust a fresh solution. It is sometimes used again for the purpose of economising, but it is more likely to result in

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waste. I cannot say that this remark applies to the bleaching of esparto where the process is carried on continuously, the bleach passing in one direction and the bleached material in the other.

Those of you who are chemists can easily verify my statements by mixing some fresh bleach of known chlorine strength with some spent bleach liquor which has been used several times. You can ascertain the effect of the spent liquor upon the fresh bleach solution by testing it periodically. You will notice a steady falling-off, especially if the solution is kept warm. This falling-off must take place in a like manner when spent or partly spent liquor is revivified by the addition of more bleach. In the case of esparto it may be different when the bleach solution is kept strong and working continuously. The process has to be conducted quickly and necessitates a strong liquor, and to throw this away still containing a lot of bleach, would be less economical than using liquor over again, although in the latter case waste is going on through by-products from previous bleachings destroying the chlorine.

There is one great danger with circulating hot bleach through stationary rags. When an attempt is made to bleach iron mordanted coloured rags, ferric oxide or magnetic oxide of iron is formed *in situ*. Under ordinary circumstances, bleach powder does not act deleteriously upon cellulose, but it is liable to do so when hot. In the presence, however, of oxide of iron, instead of bleaching the colour, the oxide acts as a conveyer of oxygen from the bleach to the cellulose in such a way as to tender it. The oxygen is supplied by the decomposition of the bleach to the ferric oxide, which in turn conveys it to the cellulose and converts it into oxycellulose.

The reduced iron is again oxidised by the bleach, and then the process is repeated, with the result that the rag is tendered instead of being bleached. I have seen iron mordanted rags mixed with other rags, the mordanted ones completely tendered, and the rest bleached but otherwise unaffected, both having undergone the same treatment.

I want you to realise that this method of hot circulation allows the air as well as the bleach to come into direct contact with the material to be bleached; whereas in the method of circulation about to be discussed, the bleaching is done by total immersion in the liquid, except at the surface of the stuff.

Let us now consider another set of conditions when liquor in the potcher is circulating whilst the bleaching is being carried on. The circulation is a valuable aid to bleaching, as it promotes the

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chemical action in various ways. It reduces the time of treatment, and tends to make the treatment much more uniform than it would otherwise be, such as in the steeping tank bleach.

In the bleaching of some stuffs, such as esparto, where the mass is kept in circulation, and where it is expedient to make the process as rapid and continuous as possible, I venture to think there must be considerable saving of time effected, due to the fact of keeping the stuff in motion. There can be no harm or danger to the material in rapidly agitating it or keeping it in motion during the time the bleach is acting. Such agitation results in economy of bleach as well as saving of time. This I have shown by actual figures to be true of the Hermite solution, but it is equally true of solutions of ordinary bleaching power whether hot or cold. It is necessary to take into consideration the cost of keeping the stuff in motion, which may amount to more than the saving in bleaching powder. Apart from this, time is an important factor, and anything that will help to get the stuff out of hand quickly is to be welcomed.

As will be seen hereafter, agitation not only accelerates the rapidity of the bleaching, but it also in a measure brings into play a somewhat different chemical reaction. The probability is that the nascent oxygen is much more effective, and that less of it is converted into ordinary oxygen or able to act on bleach products already formed.

It is easier and safer to apply heat when the stuff is properly agitated. Of course the temperature is rising from the very commencement, due to the rapid agitation, but as chemical reactions of this kind are not influenced so much at a low temperature as at a high one, every degree of rise of temperature, say between 80° and 90° Fahr., promotes a greater increase of chemical energy than each degree of rise between 50° and 60° Fahr., consequently the energy of the bleaching due to increased temperature is more marked after the agitation is conducted for some time. There is little or no benefit in warming the stuff through a few degrees only. The real benefit is derived when the stuff is raised to its safe limit, but this safe limit should on no account be exceeded.

It can hardly be claimed that any mechanical cleansing can be effected while the bleaching is actually going on, but extraneous matter and dirt, after the bleach has acted upon it, may become loosened and detached. This loosening may be assisted by mechanical agitation, but the dirt cannot be got away until the bleach is washed out.

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We have already referred to the theoretical action of bleaching powder, and endeavoured to explain it on the assumption that ozone is formed, but there is no reason for supposing that ozone alone or in conjunction with one of the hypochlorites cannot be used to great advantage in the bleaching of paper stock. If ozone is ever to come into commercial use for bleaching, its manufacture will have to be much cheapened and simplified. Of this there seems little prospect in the near future. Ozone by itself is a powerful bleaching agent, and is likely to come into commercial use as such if a cheap enough method can be devised of making it. Ozone, furthermore, accelerates the action of bleaching powder and results in a saving of chlorine. The presence of ozone and peroxide of hydrogen in the air lashed into the stuff by the action of the beater-roll must, in a measure, affect the rapidity as well as the economy of bleaching, but to what extent it is not easy to ascertain. I have heard of cylinders of compressed oxygen being used in conjunction with bleaching powder in the potcher, but have had no experience of its use.

The presence of direct sunlight in a bleach-house must also assist the bleaching, and more so when the stuff is agitated, continually exposing to the sun's rays fresh layers of pulp.

It is most essential when bleaching with hot liquor to avoid over-heating. It is often the practice to have live steam in the potcher to raise the stuff to the necessary temperature.

Care must be taken that where the steam enters the potcher there should not be local heating. This is liable to take place if the potcher circulates slowly. It is an extremely dangerous thing to rely on a man's judgment as to the temperature. If he passes his hand into the stuff and thinks it is hot enough, he may be misled, because the apparent temperature of the liquid would depend upon the temperature of the air at the time. A solution at say 80° Fahr. would, for example, feel cool in the heat of summer but hot on a winter morning, but the chemical effect would be the same summer or winter. The only way is to use the thermometer. The safest plan is to heat the potcher up to the required temperature before the addition of any bleaching liquor, and care should be taken that the steam valve does not leak, or the temperature will be further raised. For straw and esparto the maximum should be 100° Fahr., but I would suggest where it is possible 90°–95° should be the maximum. In the case of wood, 90° only should be made the maximum temperature.

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The actual amount of chlorine consumed in bleaching is largely dependent upon the temperature of the stuff. If the temperature is too high the chlorine consumed may be very high also, and the fibre at the same time will probably be injured. The fact is that to do the bleaching in a very limited time in the cold, a greater amount of bleach would have to be present than if the stuff was warmed, on account of the comparative slowness of the cold bleaching. Supposing, for the sake of argument, we required 20 lbs. of bleach to do a given amount of bleaching in two hours in the cold, and 15 lbs. to do the same at 90° Fahr. At the end of the time we might find that the cold liquor contained the equivalent of 10 lbs. unconsumed, and the hot liquor 3 lbs. Although we should have been compelled to add more liquor for the cold bleach, yet the amount actually consumed would be most in the case of the hot bleach. If, however, in the one case we bleached in the hot with such quantity that the whole is consumed at the end of the bleaching, and in the other case used a cold solution which just exhausted itself, we should find that the hot bleach would consume from 20 to 50 per cent. more bleaching powder than the cold solution.

In making the above remarks I do not wish to suggest that this rule would hold good in all cases. It is true in some cases, although perhaps not in others.

We shall have to leave a number of questions untouched. To attempt to propound a theory to account for the bleaching action of different liquids is a difficult and dangerous task. I am afraid I have already trespassed too far in this direction. I have purposely omitted all common stock knowledge such as text-books give as far as possible, and have trespassed on more debatable ground in the hope that young papermakers and chemists who take an interest in this subject may be inspired to go further and to test the validity of these remarks for themselves.

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LECTURE V.

THE INFLUENCES OF MOISTURE ON PAPER.

Effects of heat—Expansion and contraction of cellulose with change of moisture—"Sensible" moisture—The curling of paper with change of moisture—Testing for "machine" and "cross" direction by means of damping—Effects of damping.

It is a matter of common observation with all of us when reading a book in the scorching sun or close to a blazing fire, that the leaves and often the cover become bent and warped so that the book will not shut properly. If a book is left open in the sun the leaves on either side will curl up and it will be found that the uppermost leaves are the most curled, and often the bottom ones remain quite flat. When the rays of the sun meet the paper it becomes heated on the upper side, and some of the air-dry moisture is driven off by the heat. With almost all substances heat expands them, but with cellulose and like substances—which have the power of abstracting the moisture from the atmosphere and giving the same up when heated—heat has the opposite effect. Heat only has this effect by reason of it removing the moisture or dehydrating the cellulose. It is quite possible that if a paper would be kept bone dry, say, by placing it in an atmosphere over sulphuric acid and gradually raised in temperature when in this condition, that it would show a slight expansion with heat. This is not a practical question, however, for us, as under all ordinary conditions any rise in temperature means loss of moisture and consequent contraction.

Vegetable fibres vary in size according to the amount of moisture they contain. On a dry day the ultimate fibres, say of cotton, are considerably smaller, both in diameter and length, than on a damp day, and when these fibres are immersed in water they become larger. Cotton cellulose in a normal atmosphere will contain about 7 per cent. of water. Supposing we have a paper composed of cotton fibres and expose it to the rays of the sun the moisture will fall from, say, 7 per cent. to 5½ per cent

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or even 4 per cent. This fall brings about a corresponding shrinkage in the paper. If, now, we take the paper into a cool, shady place, the paper will absorb moisture until it contains 7 per cent. again, and will also return to its former size. Expose it on a damp day and its moisture may rise as high as 9 per cent., or even 10 per cent., when it will feel flimsy and sensibly damp. If we go further and expose it all night to the heavy dew, as some of you no doubt have observed, it will often be covered with beads of moisture when the surrounding objects are comparatively dry. Now take air-dry paper and lay it close to a fire for a few minutes, at a temperature sufficient to scorch the hand, it will be found that the paper has further shrunk, and also that it has lost a great deal of its flexibility. This time the paper has lost nearly the whole of its atmospheric or air-dry moisture. It will be noticed that the paper has curled in the direction of the fire. If now the paper be turned round when about half dry the paper will uncurl, and recurl only in the opposite direction. Whilst drying, it will often be noticed that the paper steams and develops a dampness. This is due to the air-dry moisture separating from the cellulose before it is able to escape into the air, and remaining on the surface of the fibres as a film of water.

The condition, as regards dampness or dryness, is a matter of everyday observation with the housewife in regard to household linen. Well-aired sheets still contain about 7 per cent. air-dry moisture. The reason that they are safe even with this amount of moisture is that at 7 per cent. the moisture is not "sensible moisture," or appreciable to the sense of touch or feel. When the moisture is sufficient to become apparent to the touch, the linen, through the presence of what we may regard as excess of moisture, becomes conductive of heat and conducts the heat away from the body, whereas well-aired linen is an insulator of heat and consequently prevents the heat of the body from escaping. Hence the danger of damp linen and the necessity for well airing. With paper also the moisture only becomes apparent to our senses (*i.e.*, feels damp) when it exceeds a certain amount, and this amount would be greater in a wood paper than in a rag paper. Although our senses only reveal the excess moisture, the cellulose or fibres of which the paper is composed is much more sensitive, and in proportion as it yields up moisture below its air-dry state, it becomes more harsh and resistent and even brittle, and loses much of its useful qualities. It is a fortunate provision of nature that the ordinary air-dry state is that state which shows up fibres their best advantage for papermaking.

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Take a sheet of paper and breathe on it, it will have the opposite effect to placing it before the fire. The edges of the paper will have curled away from the surface breathed upon. This is due to the fact that the breath is charged with moisture, which is imparted to the surface breathed upon, which, in consequence, expands and forms the *convex* surface of the curve. The heat of the fire contracts the surface nearest to it by the removal of water, and in consequence of it being less in area than the unheated surface, forms the *concave* surface of the curve. It should be noticed, therefore, that most, if not all papers under ordinary atmospheric conditions are susceptible to heat and moisture. If heated they contract and if moistened they expand, and if either of these processes is applied to one surface only, or more to one surface than the other, the paper is bound to curl.

When water is applied rapidly to one surface of a strip of paper with a brush, it often lifts itself up from the surface on which it is placed, forming an arch supported at its two ends. The application of water has the same effect as breathing on the surface, only it is much more intense.

The curve that a strip of a given length makes on being wetted on one surface only depends largely upon the thickness of the paper, and how the paper is supported. It should be noted that this curling does not take place with an unsized paper, except in a mild degree. A hard-sized paper is needed to show the result properly. The reason is that the water so soon permeates an unsized paper, and expands the other surface also.

If the paper is free to move, I have always found the curve to be the arc of a circle. When the paper is thin the curve is the arc of a small circle, and when the paper is thick the curve is the arc of a large circle. The reason for this is not far to seek. When water is applied to the surface of a paper it becomes expanded by a definite amount on the wetted surface. It might be 2 per cent. In other words, if the length of the dry side was represented by 100, the length of the wetted side would be represented by 102. A simple figure on the blackboard can be drawn to show this graphically. The wetted surface is shown as a thick line. If nothing prevented the free expansion of the wetted surface, and the dry surface resisted all expansion, the two surfaces would be represented in section by the arcs of two concentric circles, whose distance from each other is that of the thickness of the paper. By joining the two ends and extending the straight lines inwards, the point at which these bisect is the centre of the circle of which the curved paper is the arc.

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The radius of the circle formed can easily be measured tracing the curves on a piece of paper—drawing two lines tangents to the curve at any two points, for accuracy's sake as apart as the length of curve will stand, and then drawing t lines at right angles to these inwards. The point at which th lines meet is the centre of the circle. It can easily be seen comparison that the diameter of the circle increases with t thickness of the paper. The expansion of the wetted surface the same whether the paper be thick or thin, provided that t material of each and degree of wetting is the same. The thickn of the paper, other things being equal, bears a direct ratio to t diameter of the circle. The greater the coefficient of expansi of the paper the smaller the circle for any given thickness.

The lecturer has done a lot of work in order to ascerta whether the curve actually found agrees with the calculat curve, which is easily arrived at when the expansion of the pap is known.

These do not agree very closely, although they do appro: mately. The reason of this is that some of the moisture so finds its way through the body of the paper and expands that als If the ratio of the thickness to the circle can be established l experiment, the curves of papers of known thickness may l compared and their coefficient of expansion easily calculated l means of a paper coated on one surface only with a material whic will render it impervious to moisture and so prevent expansion c the unwetted side. I hope to be able to determine the coefficier of expansion of a paper on wetting from the arc of the circ produced with a paper of known thickness.

When paper is heated on one surface only, provided the hea be applied evenly and rapidly, the curvature is the same as whe wetted, only in the opposite direction.

Paper does not expand equally in all directions. In order t fully understand this it is necessary to have some knowledge c the conditions of its manufacture. The writer advanced a theory which is based upon certain observations made by Professo Tyndall and the geologist Sorby, in regard to the origin of slat cleavage. This was published (CHEMICAL NEWS, September 21st 1894). A portion of this I give in order that we may understan the effects of water in causing expansion and curling of machine made papers.

"Slaty cleavage is in no sense due to the stratification of th rock during its formation, as the planes of cleavage stand ir most cases at right angles to the bedding. Geologists are satisfie

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that it is distinct from crystalline cleavage. Mr. Sorby, the geologist, found that plates of mica are a constituent of slate rock. He found by applying pressure to a mass containing scales of oxide of iron and sand that the scales tended to set themselves at right angles to the pressure exerted, and to allow of cleavage in the direction of the plates.

"In the process of manufacture of paper the pulp as it passes on to the endless wire of the machine consists of ultimate vegetable fibres, such as cotton and linen and wood, suspended in a large volume of water. The specific gravity of these fibres is about 1.5. It must be remembered that they differ from plates of mica in that they present no plane surfaces.

"As the mass passes on to the wire it receives a lateral shake which tends to set the fibres at right angles to the force exerted by the shake. This might be at right angles to the surface of the liquid, or in a plane parallel to it. The latter direction appears to be determined partly by the force of gravity, which first of all carries the fibres through the medium in which they are suspended, and then causes them to press one on the other. The fibres are retained by the wire gauze, but the watery medium filters through. Water unable to filter through is removed by (1) suction boxes, and (2) the press rolls. The water is then removed by forces acting at right angles to the surface of the web, so that we have two sets of forces, one exerted in a direction at right angles to that in which the web is travelling, but in a plane parallel to the surface of the web, and the second in a vertical direction. These two forces acting together cause the fibres to lie in the direction in which the web is travelling."

The articles from which the above extract is taken was written with a view of establishing the theory then propounded by the lecturer, that the formation of paper in the web, or on the hand mould, is brought about by the same forces, and in the same manner as slaty cleavage in slate rock. It is here quoted to explain the "lay" of the fibres in a sheet of machine-made paper.

With machine-made papers the curvature takes place more readily in one direction, and this fact has been utilised for determining the direction the paper has come from the machine. This method is described by Herzberg in his book on "Paper-Testing," as follows:—

"If it is necessary to find which is the machine direction, and when, owing to the sheet being damaged, the direction cannot be distinguished with certainty, a circular piece, about ten centimeters (four inches) in diameter is cut out of the sample

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and allowed to float some seconds on water. It is then taken carefully, by the aid of forceps, and laid on the palm of the hand (to which it must not be allowed to stick), when the edges will be bent up until they finally overlap."

The dotted line running through all three is the direction of the web of paper on the machine.

Herzberg says: "The explanation of this test is this. The side of the paper in contact with the water absorbs moisture, causing the fibres to swell and bend the paper; as the paper expands more in the "cross" than in the "machine" direction the edges in the first-named rise."

The above appears to me to be only a partial explanation of the paper's behaviour, as I think will be made apparent after a more careful examination of the disposition of the fibres in a sheet of machine-made paper.

Mr. Little, in his book on "The Chemistry of Papermaking," describes a more simple test for determining the direction of the web in a sheet of machine-made paper. It is as follows:—Two strips are cut from a sheet, each one inch wide by four inches long; one piece is cut across the sheet and the other in the length of the sheet. They are held together between the finger and thumb at the lower end, and allowed to hang to one side. If they remain together the underneath one is cut in the machine direction. If they remain apart at their loose ends, the upper one has been cut in the direction of the machine or web.

The forces which act on a web of paper as it passes over the machine, as we have already seen, cause the fibres to lie in the direction of the web, giving the sheet greater rigidity in one direction. We know that a blind made of stout cane bound together with thread, is only slightly flexible in the direction of the strips of cane, but rolls up with great ease in the other direction. Now, a sheet of paper wetted on one side expands on the wetted side, and the paper curls in the direction in which there is the least resistance, which is across the web.

I have found it preferable not to float the disc of paper on water, but to wet it by passing it on to a well wetted pad by means of a glass plate or other flat surface. There is no danger of getting the upper side wetted by this method, and the paper is more readily removed.

I have found it somewhat difficult to obtain the inverse effect [illegible] rapidly heating a disc of machine-made paper on one surface [illegible] It is probable that the contraction, after the air-dry stage [illegible] been reached, is very slight. It has been remarked early in

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this article, that when a sheet of paper is exposed to the rays of the sun, or brought close to a fire, that the paper curls so that the concave surface is pointed towards the source of the rays of heat. If this is not performed under certain conditions, it sometimes happens that the paper is curled in the opposite direction, namely, with the convex surface facing the source of heat. This is noticed sometimes when a sheet of paper that has for some time been exposed to a somewhat damp atmosphere is brought suddenly in contact with a hot metallic surface. The paper quickly begins to curl with the ends uppermost. This is due, in my opinion, chiefly to the fact that the moisture from the heated surface which is in contact with the metal, cannot escape except by passage through the thickness of paper and from the upper surface. Immediately the paper becomes heated throughout its thickness (which takes but a few seconds), moisture begins to escape, leaving the upper surface dryer than the under surface, and so causing the paper to curl with its convex surface facing the source of heat.

An interesting effect is got by bringing a paper of medium thickness, but somewhat damper than air-dry, over a Bunsen flame or over an ordinary gas burner. The hot air from the flame impinging on the under surface of the paper, rapidly dries it, whilst the upper surface still remains damp. This causes the paper to curl down towards the flame. If the paper be retained in this position it curls back to its former shape, in consequence of the moisture leaving the upper surface when the heat has passed right through the paper.

It must be borne in mind that paper acts quite differently to fabrics when wetted. When stiffened pieces of fabric are brushed over their surface with a damp sponge or floated for a moment on water, they commence rapidly to curl, but instead of the wetted side curling outwards, as with paper, it frequently curls inwards. The only cases, so far as I am aware, in which the wetted surface curls outwards, as with paper, are those in which some material is used to dress the fabric which rapidly expands when wetted, and when this expansion is greater than the natural contraction of the fabric itself, the material curls with its wetted side inwards.

The materials used for dressing bookbinders' cloth and such like are the same as used for sizing paper, such as gelatine, glue, and starch. This leads me to suppose that the sizing materials used in paper are largely responsible for its behaviour towards water.

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In the case of paper, the curling influence of the sizing materials cannot very readily be determined, as these materials curl in the same direction as the fibre substance of the paper itself. With cloth, however, the two tend to go in opposite directions, and a lot of information may be obtained by using a stiffened fabric that has been coated with some sizing agent on one surface only. If a piece so prepared be wetted on the fabric side it curls generally with the wetted side inwards, and if coated on the filmed side it curls generally with the wetted side outwards. Sometimes a stiffened fabric when wetted on the uncoated side remains almost flat for some time. This is probably due to the contraction of wetted fabric being so feeble that it is unable to bend the coating. When the dampness has penetrated the coating is expanded and the material begins to curl.

There are important practical issues, as well as theoretical, in relation to this question. Thus there is a lot to be learned about the behaviour of bookbinders' materials when wetted with glue or paste. Bookbinders are obliged to know something about these peculiarities. When a paper is stuck to a board or rigid surface it is damp and consequently somewhat expanded, so that as it dries it draws right over the surface and takes out all the creases. A strong paper so stuck is capable of exerting enormous force as it dries or contracts by the slow application of heat. I have known a paper under these conditions to tear up a piece of stone. This is merely the effect of contraction or attempted contraction of paper due to the drying of the fibres.

Gelatine or glue—a common constituent of both fabrics and paper—expands readily in water, and if it be of good quality, on immersion in water it swells up sometimes to four times its former volume. Tub-sized papers contain often 5 per cent., and sometimes as much as 8 per cent. of gelatine. The gelatine fills the interstices of the paper. Starch is contained in most papers. It is often found to the extent of 2 per cent., and sometimes as much as 5 per cent. This probably expands on wetting, but to a more limited extent than gelatine. It is difficult to say how far these substances cause paper to curl, but it is probable that they have a lot to do with it. Any substance that is not easily permeated by water added to paper to render it waterproof may increase the curling properties of paper by allowing one surface to get damp whilst the other is unaffected. Rosin has this effect, and it is for this reason that Herzberg recommends its use when it is desired to test a machine-made

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water-leaf paper by the disc method to find the direction of the web.

It is very difficult to understand why, on the one hand, paper should expand on being wetted and a fabric should contract. It appears that the greater the expansion of the ultimate fibres themselves the greater the contraction of the cloth or fabric made from the same. This may be exemplified as follows:—When cotton is treated with very strong alkali a process goes on known as mercerisation. The cotton fibres are swollen up and largely increased in size. If a cotton fabric be treated in the same liquid the area becomes very much lessened. Mercer, who discovered this, found a contraction of about 20 per cent. The interstices, however, are largely filled up. When a cotton waterleaf paper is treated in the same way, a large increase in thickness is often noticed. If a strong solution of soda be allowed to fall on a piece of paper a blister is formed by the swelling of the paper at this point. Physically, the action of water when the paper or fabric is wetted may be regarded as the same in kind as a strong solution of caustic soda, but the action is not nearly so intense. Water is not merely taken up by the fibre as a sponge takes up water, but it probably enters into chemical union with the cellulose. There is no doubt that it altogether alters the physical properties of the fibres. It is to this change in physical properties that fibres undergo when acted on by water that we owe their peculiar power of felting into sheets of paper.

It has already been shown that the fibres of a machine-made paper lie for the most part in the direction of the web. It can easily be imagined that such a paper would tear much more readily in the direction of the web than across it.

Machine-made papers are often 25 per cent. stronger in the "cross" direction than in the "machine" direction. With common news I have known several cases where the difference is far greater. The "cross" direction is three times the strength of the "machine" direction. Such a difference is almost incredible, but it often occurs in ordinary practice. There are other reasons, however, than the mere fact that the fibres are mostly in one direction. These other reasons I hope to give you later. Paper shrinks very readily in width when on the machine, and the direction of the fibres probably has a great deal to do with the shrinkage. The paper being kept "taut" lengthwise would prevent its shrinkage in that direction, and cause an increased shrinkage in the "cross" direction. When paper is

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wetted after making it tends to assume its old shape, namely, the shape it had in the wet state when first made. It would be necessary in order to do this that it expands more in the "cross" than in the machine direction.

If the paper wetted happens to be a glazed one, the glazed surface is removed and the paper assumes both the surface and thickness it had before glazing. In other words, immersion in water undoes the work of the calender. The same thing takes place only in a milder degree in damp air. One of the causes, perhaps the chief one, for paper going back in surface after calendering is the dampness in the air causing the paper to become damp.

In order to get the watermark of the paper right in the sheet, it is often necessary to stretch the paper, either in the direction of its length or its width. This stretch probably gives the paper an increased power of curling when the same becomes damped or heated, as already explained.

The question of paper curling is, I think, an important one, and should be studied with the view of overcoming it.

In the case of a fabric, the warp and the weft resemble the strands of a piece of twine in that they consist of twisted or spun fibres or filaments. The direction of a fibre in a piece of cloth or twine is that of a helix, whereas the fibres in a piece of paper lie, for the most part, in the direction of its length and in the same plane as the surface. The difficulties already mentioned in regard to the lateral expansion of machine-made paper, which cause a disc of the same to curl in one direction, are experienced in a much less degree with hand-made paper. As we have already seen, that lateral shake of the machine, together with the forces exerted by the suction boxes, press rolls, &c., results in the fibres lying in the direction of the web, or what is known as the "machine" direction. In the process of the manufacture of paper by hand the mould receives a shake, first in one direction and then in another at right angles to the first. The fibres always try to assert themselves in one direction when shaken. If, then, the shake be exerted equally in each direction, the fibres would have no tendency to lie in any one direction, and we should expect to find them disposed in all directions throughout the sheet.

In practice this is very hard indeed to ensure. When the [redacted]ould is lifted from the vat by the operator, he gives it a few [redacted]kes—say, from side to side—as he is standing. This would [redacted] to make the fibres point in one direction. Next he gives a [redacted]of shakes in the opposite direction to the first, namely, to

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and from him. This tends to make the fibres lie in a direction at right angles to the first layer. All the time that he is shaking the water is finding its way through the wire and the fibres are subsiding. The effect of the two sets of shakes is to dispose the fibres in layers, the fibres of each layer being different in direction to the one above it. This is a great improvement on machine-made paper, but is by no means perfect, as the paper is disposed in layers instead of consisting of one mass of fibres disposed in all directions. It must be remembered also that it is almost impossible for an operator to so adjust the shakes as to make one set of fibres just compensate for its neighbour, and so produce a paper of equal strength in all directions. I think I am right in saying that even the best hand-made papers are very seldom of uniform strength in all directions. All the same for this, hand-made papers are sufficiently uniform in strength for all practical purposes, and if we could only discover some means of attaining as uniform a result on the Fourdrinier machine, provided it did not, of course, add to the cost of manufacture, a great step in advance would be accomplished in machine-made paper.

The other set of forces corresponding with the suction boxes, couch-rolls, and press-rolls comes into play with hand-made papers when the same are pressed between felts. These forces cause the fibres to lie in the same direction as the surface of the paper, and prevent them from lying in the direction of its section. If it were not for this fact, the expansion of paper when wetted would probably be much more uniform.

We next come to consider the qualifications of an ideal paper. One important qualification should be that the fibres "lay" equally in all directions. In a hand-made paper this may, to a certain extent, be accomplished in the aggregate, but when the paper is examined in section it will probably be found that layers exist of fibres disposed in opposite directions; moreover, the after-pressure of the felts causes the fibres to lie in the same plane as the surface of the paper. In an ideal paper the fibres should not only "lay" in every horizontal direction, but in all directions whether horizontal or vertical.

In spite of the fact that most papers expand when wetted, they can, in a measure, be so prepared, when circumstances demand it, as to expand or contract very little with change of moisture in the air. It is important for some purposes that paper should not alter more than $\frac{1}{16}$ in. or $\frac{1}{32}$ in. on a length of 12 inches. With paper used for taking the records of meteorological observations this is a question of some moment. Wit

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other papers the amount of expansion is not so material, provided that the expansion is the same in the two directions.

It is quite easy to represent by means of a rough sketch the relative positions of fibres in an ideal paper, showing just how the fibres should be disposed if they could be discriminated by means of a microscope in the paper. It may be taken generally that cellulose expands when wetted. I am not aware that any measurements have been made of the expansion of ultimate vegetable fibres when wetted. It appears that the ultimate fibre, say of cotton, expands more in diameter than in length.

I think there is good reason to believe, also, from the behaviour of ultimate fibre towards certain reagents under the microscope, that the increase is chiefly at the expense of the diameter of the fibre. From this we would infer that when a machine-made paper is thoroughly wetted the percentage increase is least in the "machine" direction, most in the direction of the thickness of the paper, and the percentage increase across the web lies somewhere between these two extremes. The expansion of a paper is so intimately connected with its liability to curling that the latter cannot be fully understood without a full knowledge of the former.

With chromo-lithographic work it is important that the paper should not expand with moisture, as the colours are thrown out of register. The expansion should be slight and as far as possible equal in the two directions. Moisture has a marked and beneficial effect upon some printing papers. Damping has a softening effect, as already explained; it overcomes a harshness which is objectionable. If the paper has been over-dried as it leaves the machine, damping before printing is often necessary. Damping before calendering is also needed. Paper if too dry will not take kindly to the calendering treatment. On the other hand, too much damping must be avoided. The happy medium must be aimed at, as well as absolutely uniform distribution, such as can now be accomplished by modern systems of damping done by means of a fine spray.

In conclusion, I will briefly refer to the destructive influence of water. In damp atmospheres papers are far more liable to putrefaction and decay than in dry atmospheres, more particularly when the air is both hot and damp. Under such conditions bacterial and putrefying organisms flourish. The Indian climate is destructive to papers, even hard-sized papers, not because of the heat alone, but because of the moisture in conjunction with the heat.

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LECTURE VI.

CHEMICAL RESIDUES IN PAPER.

Metallic salts—Purity of ash—Lime salts due to bleach—Influence of acidity—Discharge of lines—Presence of iron—Reasons for—Amount in raw materials—Chemistry of rusting—Prevention of rusting—Effects of iron in water on paper—Elimination of iron during manufacture—Test for iron—Iron in chemicals—In finished papers—Iron and other metallic particles.

In these lectures I am adopting what I believe to be a novel expedient. In most of them I am adopting a thesis as it were. I give you a test or subject, or perhaps it would be better to say an aspect of papermaking, for your consideration. The endeavour is made to elaborate on whatever aspect is chosen, and to garner a few at least of the facts bearing on the question at issue. Some of the questions I venture to think are novel, at any rate as forming the subject of a lecture. They tread on more or less debatable grounds, but this we cannot help, because if we avoid debatable grounds we shall make very little progress. If we are to treat only of well-tried and well-tested questions that have been written upon times without number, we might as well, to use a slang expression, shut up shop as far as this course of lectures is concerned. I should then merely draw them to a close by referring you to current literature on the subject. But I am engaged to come here and put before you, to the best of my ability, fresh subject-matter, or. at any rate, fresh aspects of papermaking for your consideration. The extent to which you may profit by it will depend very largely as to whether it does what Carlyle declared to be that which is the greatest help that can be conferred upon a man. It should help you to help yourselves. If by these lectures you are better able to acquire further knowledge for yourselves some lasting benefit may accrue, but if you go away and think no more about them, whether they have any

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intrinsic merit in themselves or no, I can hold out no hopes that you will be benefited.

I admit that these lectures may be over the heads of some of those who attend, but this is inevitable in a mixed class. It is for this reason that I have decided during the actual delivery of the lectures to give you more elementary details than the text contains, and in many places not to stick to the text at all, in fact, often to branch off into other subjects which may appear more palatable and suitable to the individual members. By this system you have really a twofold advantage, for you have the advantage of hearing me speak upon more elementary details, and joining in a discussion afterwards, and you have the opportunity of reading through copies of the proofs, and discussing them afterwards, should you desire to do so.

The subject of this lecture is perhaps a difficult one, but is important and at the same time fascinating, both to the chemist and to the papermaker. It more particularly interests makers of high-class papers. My attempt is here not so much to give a lot of solid information as to indicate by what little information is herein given a method by which further may be acquired.

It is important, at any rate to the maker of photographic paper, that his paper should contain little or no metallic salts. In order to avoid the introduction of metallic salts he must have a ready means of testing his products during their various stages of preparation.

There is the question of ash in pure paper. If the ash is to be kept down, perhaps for the purpose of complying with some specification, the processes that give rise to the ash should be traced, and when the causes of the introduction or removal of ash are known, the exact quantity, even in pure papers, which are supposed to contain none, can be more or less controlled. I have known a paper to contain 10 per cent. of ash, not through the clay or other mineral being added, but through the peculiar power that the said fibre possessed in condensing the lime salts from the bleach solution added to bleach it. This of course is an extreme case.

Then we have the question of the exact condition of the paper as regards so-called acidity or alkalinity, with which I hope to deal in a future lecture. This, again, is a question of chemical residues.

Furthermore, we have the question which has caused so much trouble at different times of papers affecting printers' inks or printers' inks affecting papers, so as to give rise to a pungent

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smell. This is a difficult and intricate one, and one only upon which some chemist skilled in the detection of very minute chemical residues could form any opinion. While admitting that paper may be prepared so as to overcome this nuisance, it must be admitted that the blame, if any, rests as much with the inkmaker, or the printer who will insist on using a common-made ink, as with the papermaker, because a remedy is as often effected by changing the ink as by changing the paper.

The same question has also been raised in connection with certain well-known makes of writing inks, as being unnecessarily penetrating with tub-sized papers, even with the best makes. It would seem that in this last-mentioned case the inkmaker should do what he can to meet the difficulties of the papermaker; whether he has done so I have no means of judging.

Then we have the qualities of minute chemical residues in papers in their effect upon analine inks. The faint lines ruled upon some foolscap paper appear to fade away fairly rapidly on some common papers. I should have liked to suggest that it is confined to the common paper. It appears to take place more readily when the papers are allowed to get even the least bit damp. The question again arises—Is it the fault of the papers, or is it due to the fugitiveness of the colour used? It may be either or both. We certainly do not want to find after a few years that our press copies of type-written letters have faded away, so that they are no longer legible. Under certain conditions this undoubtedly does take place, both with the copy and the original, whereas, under other conditions, as far as we at present know, they remain permanent, or nearly so. Sometimes the press copies or originals are inclined to bleed or become blurred, and can only be read with great difficulty. The Italian Government have taken a wise precaution in prohibiting the engrossing of legal documents by means of the typewriter. In the United States it is a very common custom to draft legal documents by means of the type-writer. It will be interesting to see what attitude they will take now that they meditate the establishment of a State laboratory to go into such matters.

We will now trace the presence of iron as a metallic impurity through the different stages of papermaking.

*Doubtless many of us are not aware that the salts of iron are in some way, at present unexplained, intimately connected

* This article is largely abstracted from an article on the presence of iron in paper, which I originally contributed to the PAPER-MAKER.

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with the life and growth of the animal and vegetable kingdom around us. All the members of the plant world that elaborate for themselves their food from the inorganic constituents of the soil, and from the invisible nourishing gases of the atmosphere, are possessed of a green substance known as "chlorophyll," which enables them to convert these inorganic lifeless bodies into a part of their own living structure. This wonderful substance "chlorophyll," which seems to form a chain between the living and the dead, invariably contains iron salts. Without iron salts plants would be divested of their green colour. A very simple experiment illustrates this. If we take a few grains of Indian corn and place them in water which contains all the necessary ingredients for their growth, with the simple exception of iron, the Indian corn will sprout and grow to a certain degree, but it will be found devoid of colour. If the surface of the leaf be touched with the solution of a salt of iron, or if the solution be added to the water, the leaves will develop the green colour due to the presence of chlorophyll, which will enable the plants to continue their growth. With retted flax and fabrics that are more or less cleansed of chlorophyll, that remaining is easily recognised by the brilliant blue venation when the chemical reagent for iron is applied.

The blood of animals contains a red substance known as hæmoglobin, which gives to the blood its characteristic colour. This substance invariably contains iron, which amounts to 0.42 per cent. on the weight of the hæmoglobin. Here, again, iron has a most important function to perform.

The bearing that the above facts have on the subject of this lecture are soon made manifest.

All substances of animal and vegetable origin are found, as might well be inferred from the above, to contain iron. Paper consists of substances that are mostly of vegetable origin: thus cotton, linen, wood, straw, esparto, and other vegetable fibres, as well as such substances as starch and rosin. It also contains substances of animal origin, the chief of which is gelatine.

The chemicals used also are found to contain some iron salts, so that we may safely say that all materials used in the manufacture of paper contain iron.

When an organic substance is burnt the iron remains in the ash, and can be recognised by dissolving in a little nitric acid, adding water, filtering, and adding a few drops of potassium ferrocyanide solution, when a blue coloration is produced due to the formation of Prussian blue. The depth of this coloration is a

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measure of the amount of iron present. The amount of iron can be exactly determined by comparison with a solution containing a known quantity of iron.

The following determinations will be found useful for reference. All raw materials are subject to a considerable variation in the amount of iron they contain, but these figures are fairly representative, being the result of a large number of analyses.

	Parts of iron per hundred thousand.
Cotton wool	6.0
New pieces	1.0
Unbleached cotton	14.0
New canvas	18.0
Rag dust	175.0
Dirty rags	65.0
Clean rags	25.0
Rosin size	.45
Crystal alum, pure recrystallised	.043
Sulphate of alumina	.35
Mechanical wood (aspen) ..	10.0
Aspen wood	5.0
Bleached sulphite wood pulp ..	8.0
Bleached pulp from aspen wood..	12.0

Thus we see that pure cellulose, as cotton wool, new pieces, or any other form, contains little iron.

With flax the extent of the retting and after-treatment would largely determine the amount of iron as a residue. It follows then that with flax or linen, the more the fibres are cleansed of iron cellulose the less the iron. With raw materials, such as skins, the more thorough the treatment for the removal of blood and hair the less the iron as a residue.

But rags contain a very considerable quantity on account of the dirt and foreign matter containing iron with which they are contaminated. That this dirt contains a large amount of iron is shown by the very large quantity found in rag dust. We must not look on rag dust as consisting of dirt only, as it contains on an average about 50 per cent. of cellulose. The iron which rags contain due to the dirt is not so difficult of removal as that natural to the fibre. On evaporating down some of the spent liquors from boiling rags, I found considerable quantities of iron, sufficient to account for the loss of iron that the rags sustain by this treatment.

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a very large amount of iron, When these rags are boiled in in combination with the iron remains firmly embedded in the magnetic oxide of iron. When solution, especially when the bleach is used in warm solution, the rags are considerably rotten. The explanation of Bleaching powder solution, acts on the organic colouring into colourless soluble products. on the cellulose. When, contain oxide of iron the action is different. oxide, giving up its oxygen to the cellulose, converting it into oxycellulose, which results in the The ferrous oxide is converted back supplied to it by the bleaching undergoes a similar cycle of changes, being and so merely acts as a bearer of The importance of the removal of iron cannot be over-estimated. This is with muriatic acid, whereby the into soluble ferric chloride, The removal of iron is often immediately after boiling. No doubt by boiling and washing, but to remove, even on prolonged is to give the rags a good souring is much more readily removed. much less acted on by the bleach better colour.

found in papers is derived from washers, &c., with which the the metallic iron has first to be can be imbedded in, or discolour consider. What is rust? How is it prevented?

supposed to be ferric oxide (Fe_2O_3), iron. Recent researches, how- contains a large amount Research has also revealed the fact deprived of carbonic acid gas, neither moisture. It seems also most

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probable that iron cannot rust even in pure oxygen. The explanation of this is plain. Iron shares with all other metals the property of condensing on its surface a film of moisture. Carbonic acid gas is very soluble in water, therefore the film of metallic iron contains a considerable quantity of carbonic acid, derived from the atmosphere. Ordinary air contains 4 parts of carbonic acid (CO_2) per 10,000. Carbonic acid in contact with iron becomes reduced to carbonic oxide (CO), at the same time oxidising the iron.

Carbonic oxide on meeting with the oxygen of the atmosphere is oxidised again to carbonic acid, and so the carbonic acid merely acts as a bearer of oxygen from the atmosphere, and the film of water is the medium through which it is conveyed.

The action is really more complicated than this, for a small quantity of ammonia is formed, due to the combination of the hydrogen of the water with the nitrogen of the atmosphere.

We often notice that a bright surface of iron is some time before it begins to rust, but that when once the action is started it goes on with ever-increasing rapidity. The reason of this is that in course of time we have a layer of magnetic oxide, and a layer of ferric oxide. These two layers set up a galvanic action which results in the more rapid oxidation of the metal.

Now we know the exact conditions which attend the formation of rust we are able to find a remedy. Caustic soda solution has a great affinity for carbonic acid, combining with it to form sodium carbonate. If we have any iron tanks or boilers lying empty, and we wish to prevent the formation of rust, we must fill them with water containing a little caustic soda, which seizes hold of the carbonic acid gas before it has a chance of reaching the iron.

We now see why rusting is worse at or near the surface of the water in an iron tank.

It follows from the above that there need be no fear of rusting of boilers that are constantly used for alkali boils.

Water used for washing is likely to contain iron derived from the rusting of the tanks in which it is stored, and this is often found to be the case. I found that water of the following composition—

15 grains of carbonate of lime per gallon,
6 grains of sulphate of lime per gallon,
5 parts of iron per ten million of water,

on being left in contact with 1 per cent. of its weight of iron for three days, contained at the end of that time 50 parts per 10

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million. The metallic iron was at the bottom of the vessel containing the water.

The danger of using water contaminated with even traces of iron is that cellulose has a great affinity for iron salts, which it removes even from very dilute solutions. The following experiment exemplifies this :—

Some pure cellulose was placed in twelve times its weight of water, the water contained 10 parts of iron per 10,000. On taking out and thoroughly washing, the cellulose was found to contain one-third of the iron.

A piece of paper consisting of cotton and linen was similarly treated, and was found to have abstracted half the iron from this very dilute solution.

Before treatment the paper contained 15 parts of iron per 100,000, after treatment it contained 70 parts per 100,000. A large number of other trials might be cited, but they all show that cellulose has the power of attracting iron even in very dilute solutions.

Unfortunately iron has the power of imparting a brownish tint to cellulose when the former is present even in very minute quantities.

We would expect to find that the iron natural to the fibre is uniformly distributed throughout the whole mass of the fibre. With cotton, which belongs to the seed hairs, this is the case, but with linen this is not so. Let us take a piece of linen fabric and immerse it in water containing 1 per cent. of potassium ferrocyanide and a few drops of nitric acid; in three hours we shall find that the fibres have developed a blue colour; some of the filaments will be found to be much bluer than others. The flax fibre has to undergo a process of retting, whereby the green pulpy matter containing the chlorophyll is removed from the fibre. If this process is not complete, some of the iron contained in the chlorophyll may become part and parcel of the fibre, even after the chlorophyll has been destroyed. This is bound to result in an irregular distribution of the iron in the different fibres.

Some lignified fibres contain a large amount of iron, which, however, is readily removed, as it is in combination with substances that are removed by the chemical treatment. The following is a typical instance :—

A sample of Sunn hemp fibre contained 250 parts of iron per 100,000.

The paper made from the same contained only 6 parts per 100,000.

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We next come to consider the several ingredients added to the fibre in the course of manufacture.

Alum and sulphate of alumina. For a long time these two compounds entered into keen competition. Sulphate of alumina has for many years been cheaper *pro rata* than alum, but it was not used for high-class papers, as it contained both free acid and a considerable quantity of iron. Many attempts were made to remove the last traces of iron, with the result, now, that sulphate of alumina can be obtained nearly as free from iron as crystal alum, if we except, perhaps, Turkey red alum, which is purified from iron by repeated crystallisation. This is of very great importance, for the greater part of the alum finds its way into the finished paper.

The iron present in starch is so small that it may be neglected.

The question arises, does the paper derive any iron from the various iron fittings of the paper machine? I endeavoured to solve this question by taking pieces of paper at different stages of manufacture, and have not yet been able to detect any increase in the amount of iron as the paper passes over the machine.

Thus, in one instance, I found a piece torn off immediately after passing through second press rolls contained 7 parts of iron per 100,000.

The same after it had passed over iron drying cylinder, 7 parts of iron per 100,000.

The best method of determining whether tub-sizing increases the amount of iron is to take a piece of the water-leaf and a piece of the paper, after tub-sizing, and determine the amount of iron in each. The difference will represent the amount of iron due to gelatine and alum in the trough.

If we know the amount of iron in the alum and the proportion of alum we are using, we can soon calculate what is due to the gelatine. The amount of iron in the gelatine varies considerably with its quality and source.

The iron in finished paper can be shown in a rough-and-ready way by cutting the pieces under examination into strips and immersing them in 1 per cent. solution of potassium ferrocyanide, together with a few drops of nitric acid, in a photograph dish. The dish should be covered over with a glass plate and the samples left in for three hours, at the end of which time they will all have developed a blue colour, in depth equal to the amount of iron present. The samples should be washed and dried. The blue colour thus produced is very permanent, and the samples can be kept for years without fading. This method thus affords us a

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means of determining whether the papers made from time to time undergo any change in the amount of iron they contain. The very compound here produced is used in the manufacture of paper for giving it a blue tint. It is well known that papers coloured with Prussian blue fade very rapidly under certain conditions. The Prussian blue is added to the pulp as a precipitate, whereas the trace of Prussian blue formed by adding potassium ferrocyanide to a paper containing a trace of iron is formed *in situ*. A great deal of iron, undoubtedly, has thoroughly penetrated into the cell wall of the fibre and has become fixed and largely converted into ferric oxide. The Prussian blue is then formed within the cell wall, and so is imprisoned, thus rendering it much less sensitive to light.

For an accurate determination, however, this method cannot be made use of. If the paper under examination is not white, if, for instance, it has a yellow tint, the blue developed is partially neutralised by the yellow, and the paper appears to contain less iron. The iron must then be estimated by taking a weighed quantity of the paper, burning it, and determining the iron either by the colorimetric or gravimetric method.

The following are determinations made in these methods :—

	Parts of Iron per 100,000.
Iron in News—	
8 different samples analysed—	
Greatest amount	60.0
Least amount	4.0
Mean	39.6
Periodicals and Journals—	
13 different samples analysed—	
Greatest amount	30.0
Least amount	3.0
Mean	16.7
Book Papers—	
4 different samples analysed—	
Greatest amount	25.0
Least amount	8.0
Mean	12.5
Mean of all analyses of all paper tested	22.9

The mean is not the figure midway between the greatest and the least, but represents the total iron in all the analyses divided by the number of analyses.

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The samples were taken from among the leading papers. These results show that the better-class papers contain much less iron than the lower class, and this is what we might well expect.

Paper frequently contains metallic particles, and many of these consist of iron. Some of these particles would escape detection, as they are too small to be distinguished. When, however, the paper is immersed in the acidulated potassium ferrocyanide solution, the particles of metallic iron are rendered evident by the production of intensely blue spots.

Often, however, metallic particles are due to the presence of brass derived from the beater knives, and often from the buttons in the rags, in which case the paper on immersion in the same reagent will develop chocolate-coloured spots, showing the presence of copper.

It is important to have a ready means of determining the presence of metallic particles as well as metallic salts. Iron particles sometimes found in papers are objectionable, as they may give rise to iron mould, especially if the paper gets at all damp. This mould may eat away the paper as it does a fabric. Brass is less objectionable in this respect, although it should not be allowed to enter into better-class papers. Zinc is sometimes found on the rims of buttons. I published an easy method for the detection of brass or copper particles in the CHEMICAL NEWS. It merely consisted in placing a bead of water, in which nitrate of silver was dissolved, over the suspected particle, and covering same with a watch glass, and leaving it in a dark place; if brass or copper were present arborescent crystals of metallic silver soon grew on the spot where the brass particle was, and copper went into solution; with iron no change took place.

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LECTURE VII.

*CHEMICAL RESIDUES IN PAPERS *(continued)*.

Definition of paper—Contamination of paper from raw materials—Lime boiling—Removal by subsequent washing—Impure caustic—Fixation of lime from water by fibres—Effects of different materials added to the chest—Mode of testing papers—Indicators—Chemical condition of paper — Soluble constituents — Insoluble constituents — Effects of metallic residues at high temperatures—Behaviour of iodide paper—Acidity and alkalinity of different papers.

PAPER has been defined by some writer as being an aqueous deposit of any vegetable fibre. Perhaps a more adequate and brief definition could hardly be given. It appears, however, to require a certain limitation in order that the definition may not include certain articles which could not be classed as paper. In order to do this, I should define paper as the aqueous deposit of any vegetable fibre in the form of a web or sheet. To leave out the word vegetable appears to be a mistake. Although woollen and silk rags may be deposited, and also asbestos fibres, they can hardly be classed as forming the basis of paper.

In addition to that which forms the fibrous basis or network, namely, the vegetable fibre deposited from its suspension in water, we have other materials which almost invariably form part of the paper, among which are gelatine, starch, rosin-size, alum, soap, and minerals.

The raw material during its preparatory treatment undergoes a course of chemical treatment to free it from that which is useless.

The resulting material, which consists of some form of cellulose, acts as a magnet to the various chemicals used in its preparation. These are more or less retained by the paper, and play an important part in its after-life and history.

* The Author discussed this subject at some length in the columns of the PAPER-MAKER as an outcome of his paper on "The Acid Action of Drawing Papers," which was read before the Chemical Society as a criticism of certain conclusions arrived at by Professor Hartley, F R.S., in regard to Whatman's Drawing Papers.

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In addition to the above substances, which steal into the finished paper by being hidden and occluded by the cell-wall of the paper, should be mentioned those substances which are added to the pulp, or the unfinished paper, to give it weight, or some new property. The latter often exist in larger quantities than the former, but they are generally associated with the fibre in a different manner, and appear to have a greater external influence, such as upon substances used to coat the paper. Those substances which are embodied in the cell-wall appear to exert a more important influence upon the fibre itself.

We will attempt at first to briefly trace the former substances. Most raw materials are subjected to an alkaline treatment for the removal of (*a*) in the case of such materials as cotton, linen, rags, &c., foreign matter, with which the fibre is contaminated; (*b*) in the cases of such substances as wood, straw, and esparto, for the removal of substances that are not foreign to the raw material, but are in combination with it, and form part of the original fibre substance. The cellulose residuum, after the removal of these substances, has a much greater power of absorbing soluble salts and bases than those classed under (*a*). Jute bagging and unbleached linen rags belong to both classes, as they both contain a large amount of contaminating matter, and also substances in combination with their respective cellulose, but capable of partial removal by the alkaline treatment.

The alkaline treatment above referred to is generally either that of boiling with lime or caustic soda. Lime is seldom used, except when class (*a*) is under treatment. The lime enters into combination with the foreign matter to form an insoluble soap, and is used in revolving boilers. The compounds formed are insoluble soaps which, being friable, are dislodged from the fibre by the mechanical agitation due to the motion of the boiler. Provided that the after-processes of washing are thorough, very little lime is left in contact with the material; its removal is always associated with a corresponding loss of those foreign substances with which it has entered into combination.

The caustic soda forms soluble salts, which enter into solution in the boiling liquor at the time of their formation. It, however, contains impurities, unless the highest grades are used, which militate against its beneficial action; among them may be mentioned iron and alumina. The former is insoluble in caustic soda solution at the strength at which it is used, and can only be associated with the fibrous material as ferric oxide or magnetic oxide.

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It may or may not be readily removed by the subsequent mechanical treatment during washing. The latter substance, alumina, may be contained in the boiling liquor as sodium aluminate. If the caustic liquor is not very strong, and the water used for its mixture and dilution prior to coming in contact with the fibre contains a considerable quantity of lime salts, the lime is rendered insoluble, and forms a flocculent precipitate of the hydrate, which, to a large extent, becomes intermingled with the fibre. If the alumina is allowed to gain access to the fibre as sodium alumina, it is absorbed and condensed by the former during the treatment. It is highly probable that sodium aluminate dissociates readily *in situ*, and produces alumina within the cell-wall. This being the case, no amount of chemical treatment or washing will remove it, and therefore it finds its way into the finished paper as an insoluble base. Some papers, even after thorough washing, are found to contain large amounts of bases, which are, for the most part, insoluble fixed bases incapable of removal by treatment in water alone, and not by any means easy to remove by treatment with acids.

Low grade caustic sodas contain impurities which militate against the chemical action of the free caustic. This has been referred to in a previous lecture. It should be pointed out, however, that when, say, 60 per cent. caustic is dissolved up in a copper, and diluted to, say, 16° Twaddle with hard water, and pumped to a store tank, as is often the case in practice, much of the impurity is removed as scum or sediment, so that the clear liquor as drawn from the store tank is considerably purified. Where low grade caustic is used this *modus operandi* should certainly be resorted to, as it adds considerably to the purity of the alkali, and as a consequence to the economy of boiling.

When the unbleached but boiled material is subjected to the action of bleaching powder, the lime salts are readily condensed in some cases. Notice that lime salts are condensed by cellulose residues, such as in the case of bleaching with calcium hypochlorite, whereas the lime salts are not condensed in a lime boil, but enter instead into combination with the encrusting matter, for subsequent removal in an insoluble form by washing. The lime absorbed by the fibre, if in contact with the atmosphere, is converted into carbonate of lime, which is nearly insoluble. I have found by comparing the ash before and after bleaching, a very large increase, due to the formation of carbonate of lime with some fibres containing low yields of cellulose. With materials belonging to class (*a*), little or no increase is noticed, but in class

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(*b*), where the residuum often contains considerable quantities of oxycellulose, the gain is very marked. I have found where the bleach consumed in one case amounted to about 30 per cent. on the raw fibre, a gain of $7\frac{1}{2}$ per cent. in the ash after bleaching. With the purest form of cotton and linen rags the ash is found to be considerably above the normal of raw cotton. The power that cellulose has of retaining soluble salts is shown when stuff containing a considerable excess of bleaching powder is copiously washed in the beater or breaker. If the stuff, and also the solution that it contains, be frequently tested with a solution containing soluble starch and potassium iodide. At a point where the water no longer gives the reaction, the stuff will still be found to yield the blue colour, and this, after the washing has been continued for a considerable time, and even after the stuff has had ample opportunity of assimilating with the water. If the washing be stopped for some time, the water after a bit is found to contain some of the lime salts. It happens sometimes that the washing is too rapidly done to remove the whole of the bleach, in which case it is retained by the fibre. It is not long before the stuff fails to give the blue coloration with starch and potassium iodide, due to the fact that the whole of the free chloride present has expended itself.

The lime salts are readily fixed in the fibre by the bicarbonate of lime present in the water used for washing. When stuff containing bleaching powder, no matter whether the free chloride has been expended or not, comes in contact with hard water containing bicarbonate of lime, the free lime contained in the cell-wall of the fibre is converted into carbonate of lime *in situ* by abstracting carbonic acid from the water. The formation of calcium carbonate *in situ* is attended by the formation of a corresponding quantity of calcium carbonate as a precipitate in the solution, provided there be no free carbonic acid in the water. Thus:—

In fibre. In water. In fibre. In water.

$$CaO + CaO(CO_2)_2 = CaCO_3 + CaCO_3$$

With regard to the bleaching powder itself ($Ca(ClO)_2$), the free carbonic acid, and probably that combined to form calcium bicarbonate, combines with the calcium to form the carbonate, and liberates hypochlorous acid. Thus:—

$$Ca(ClO)_2 + CO_2 + H_2O = CaCO_3 + 2HClO.$$

It is doubtful to what extent the bicarbonate of lime will yield up carbonic acid to bring about this change, but it appears to do it, to a large extent, with some waters.

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The explanation of the assimilation of lime salts by pulp whilst bleaching and washing may be summarised as follows:—The cellulose absorbs the so-called calcium hypochlorite from its solution. On contact with hard water whilst washing, these salts, before their removal can be effected, are converted into insoluble calcium carbonate by the carbonic acid in the water. That which passes away is often found to be, for the most part, hypochlorous acid. This action is also assisted by the carbonic acid contained in the air, especially when the material is agitated during the treatment.

If the bleach in the beater is neutralised with an antichlor, it generally adds to the alkalinity of the pulp. Thus, for instance, when sodium sulphite is used—the commercial salt itself being an alkaline substance—the alkalinity is increased. To reduce the alkalinity sodium bisulphite may be used. This salt oxidises to sodium sulphate and sulphuric acid, thus:—

$$2Na_2SO_3SO_2 + 3O_2 = 2Na_2SO_4 + 2H_2SO_4$$

The sulphuric acid so formed combines with some of the bases present.

When rosin size is used the resulting compounds are theoretically neutral; but it seldom happens that the rosin soap and alum are used in equivalent quantities. According to the equation, sodium aluminate should be formed. The latter substance is hardly likely to be formed, as the hard water present would bring about the precipitation of alumina. The chemical changes which take place in the chest are exceedingly complicated, and vary enormously according to conditions.

The treatment of paper stock from the beginning is almost entirely basic, and the only substance likely to overcome this basicity is the alum or sulphate of alumina.

I will take an individual case in detail, in order to see how far the basic and acid substances are balanced.

The following case is one in which bisulphite of soda was used as an antichlor, and the bleaching done in the beater. The chest contained 32 cwts. of dry stuff.

The alum was added as a 20 per cent. solution of sulphate of alumina, which was added to the stuff as follows:—

To the chest	.. .. ..	45 gallons.
To the machine	.. ..	22 „
To the gelatine	.. ..	20 „

The sulphate of alumina was used up in the following ways in neutralising the basic substances:—

(1) Used up in neutralising hardness of water. Water contained 17 grains of carbonate of lime per gallon. The stuff in the

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chest contained 4 per cent. of fibre and 96 per cent. water. For 32 cwts. of fibre we should then have $\frac{32 \times 100}{4} = 800$ cwts., say 90,000 lbs. of water. Which would contain $\frac{17}{70{,}000}$ of 90,000 = 153,000 grains of carbonate of lime.

Now, 114 parts of sulphate of alumina are required for each 100 parts of lime. Therefore, we should require $\frac{153{,}000 \times 114}{100}$ = 174,000 grains of sulphate of alumina, or 25 lbs. of sulphate of alumina.

(2) Sulphate of alumina to neutralise rosin size. Seven gallons of rosin size = 70 lbs. at 10 per cent., sodium carbonate = 7 lbs. of carbonate, which = 8 lbs. of sulphate of alumina.

Alum in chest and in machine added, equal together 57 gallons at 20 per cent. = 154 lbs. of sulphate of alumina.

Nos. (1) and (2) above together consumed 33 lbs. The amount of alum we should expect to find in excess would be 154 – 33 = 121 lbs. free alum. Therefore, back-water might contain 121 in 90,000 = .134 per cent. sulphate alumina, equal to $\frac{.134 \times 98}{114}$ = .115 per cent. sulphuric acid.

The paper after passing through press rolls was found to consist of—

27 per cent. dry fibre,
73 per cent. water.

The wet paper was found to contain alum equal to 0.26 per cent. of sulphuric acid on the dry weight of fibre, or equal to .07 per cent. on the water contained therein.

It is probable that the back-water contained less alum than the above figures, as cellulose has a considerable affinity for it, which it abstracts from the back-water.

By calculation we find the figure should be .115 per cent., by estimation the figure is found to be .070 per cent. in solution.

The difference is undoubtedly due to not making allowances for the bases in the pulp before it entered the chest.

We next pass on to the sulphate of alumina added to the animal size.

20.0 gallons at 20 per cent. = 40 lbs. sulphate alumina.

$\frac{40 \times 98}{114}$ = 34 lbs. sulphuric acid.

36 cwts. of sized paper = 4,032 lbs.

4,032 lbs. = 34 lbs. = .8 per cent. on the weight of the paper.

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The quantity of sulphate of alumina added to the size can be fairly well determined by taking the acidity of the paper before and after sizing. It must be borne in mind that the alum added to the animal size when tub-sizing is resorted to all enters the paper, whereas that added to the chest or to stuff before it passes into the machine is diluted with the water in which the fibres are suspended, and its retention is due to two causes, (1) the condensing power that cellulose has upon alum in solution, (2) the moisture contained in the stuff after it passes the second press. In the case of the above-cited fibre, we find that the water was exhausted by .0269 per cent., due to this cause.

This would add to the acidity of the paper $\frac{.026 \times 100}{27}$ = say .1 per cent. acidity.

With regard to the latter cause, provided that the dilution in the chest and the amount of water contained in the paper after passing the second press be known, and providing no water is added to the back-water other than that derived from the chest, we can readily calculate the amount of alum retained, and the acidity of the paper due to this cause.

Supposing we have in the chest 1 part of dry fibre to 25 of water, as above, and that the paper also contains 27 per cent. dry fibre and 73 per cent. water; after the second press, taking the amount of alum we find in excess in the chest, 101 lbs. to 19,600 lbs. of dry fibre, the calculation is simply as follows:—

$\frac{101 \times 100 \times 100 \times 100}{25 \times 19{,}600 \times 27}$ =.13 per cent. sulphate of alumina retained by paper due to cause (2).

This would add to the acidity of the paper to the extent of $\frac{.13 \times 98}{114}$ = .11 per cent. in terms of H_2SO_4

In this particular case, then, by far the greater part of the acidity of the paper is due to the sulphate of alumina added to the gelatine for tub-sizing, although this only formed a minor part of the total quantity of the sulphate of alumina used altogether.

The following is a summary of another trial. 45 gallons of 20 per cent. of sulphate of alumina used in all:—

	Gallons.
7 gallons of rosin soap consumed	6.88
30 of ordinary hard soap consumed	4.55
7,168 gallons of hard water consumed	20.45
Balance of sulphate of alumina	13.12
	45.00

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The balance is partly made up in neutralising the bases in the pulp, but there was a sufficient amount of sulphate of alumina remaining to give the water-leaf an acid reaction.

Expressed in percentage or total sulphate of alumina used, the consumption is as follows :—

45.5	per cent.	consumed	by hard water.
15.3	„	„	„ rosin soap.
10.1	„	„	„ hard soap.
29.1	„	„	„ bases and free.
100·0	per cent.		

The unconsumed sulphate in this case can hardly be said to be wasted, since it is necessary to have an excess to ensure complete precipitation of the rosin, and a rosin-sized paper should always be finished slightly acid to get the maximum sizing effect.

Most papermakers would be surprised to hear that it is a matter of the most careful adjustment to ensure that a paper does not give either an acid or an alkaline reaction. With paper that is used for a great many purposes it is a matter of indifference whether it be neutral or not, but with some paper a little care in this respect would add largely to its value and utility. I desire merely in this article to draw attention to this matter, and to show as far as possible what influence the various processes to which the raw materials are subjected and the various ingredients used in the course of manufacture have upon the finished product. I shall attempt also to give some ready means for the examination of papers, and to show their behaviour with certain indicators.

Some word is wanting which should express the relationship of a paper to indicators, such as litmus and methyl orange—in short, that will express the three conditions at once—(1) acidity, (2) neutrality, (3) alkalinity. It might be called chemical condition, but even this would by no means properly define the condition wanted.

There is the strongest objection to the use of the three terms separately.

If we find that a certain paper, when placing on a drop of weak neutral litmus, turns the same red, are we right in saying that the paper is acid because acids turn litmus red? We immerse the same paper in a carefully neutralised solution of congo red, and we find that the latter will go the same colour that it would if an alkali was added to it. It would appear, then, that the paper was alkaline.

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We try the same with methyl orange, and this also indicates that the paper is alkaline. Shall we call the paper acid or alkaline? This is a question that has never been closely studied. The truth is that acidity or alkalinity is only a matter of degree, as heat and cold. One acid is stronger than another and is capable of replacing it. Also one alkali or base is stronger than another. It may be said that the stronger acid is more acid than the weaker, also that the stronger base is more alkaline than the weaker base. In paper we have certain substances always present, which consist of a mixture of an acid and a base. The same substance may play the part of an acid or a base, according as the substance with which it is in combination is more acid or basic than itself. Alumina is dissolved by soda to form sodium aluminate, when it acts the part of an acid substance. If sulphuric acid is added to this, which is a much more powerful acid substance than alumina, the alumina is first of all turned out by the sulphuric acid, and if further acid be added it turns over and becomes the base, and enters into combination with the sulphuric acid to form sulphate of alumina. There is a substance known as normal alumina sulphate. When these two substances are compared the former is strongly alkaline to the latter, or the latter acid is compared with the former. The former substance is neutral to litmus and the latter to congo red. Cross and Bevan found that the neutral point with methyl orange is reached when there is present two molecules of alumina to five of sulphuric acid. With congo red the ratio is two of the former to six of the latter. With a paper like the one described, if alumina and sulphates be present (to which there is seldom an exception), the difference in the action of the three indicators is easily explained. And by the use of these three indicators on the same paper, a very fair idea is obtained as to what I am forced to call, for want of a better name, "the chemical condition of the paper." The paper being alkaline to congo red shows that no free acid is present, the paper being alkaline to methyl orange shows that there must be less sulphuric acid in combination with alumina than is expressed by the ratio $2Al_2O_3 5SO_3$. The fact that the paper is acid to litmus points to the probability of the paper containing a low sulphate of alumina, although, if the whole of the alumina were free, or even some of it in combination with soda, the paper might still give an acid reaction with litmus. Our ultimate object in thoroughly understanding the behaviour of paper in regard to various indicators is to throw light upon the action of the paper in regard to different colours and inks. It must be borne in mind,

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also, that a knowledge of the constitution of the chemicals in the paper will be of help to us in ascertaining whether any chemical change is likely to take place in the paper itself which may result in the paper becoming discoloured and rotten when kept for a great length of time.

When congo red is added to a solution of alum or sulphate of alumina it does not give the acid reaction unless there be free acid present. The same holds good with a paper. If a drop of congo red be placed on a paper and it turns blue, the paper contains free acid; if it is alkaline to methyl orange but acid to litmus it probably contains a basic sulphate of alumina; if it is basic to litmus, which is often the case, but is found to contain both sulphate and alumina, there is no basic sulphate of alumina present. Alumina may be present in the free state, and the sulphuric acid in combination with lime salts as sulphate. When a soluble base is added to sulphate of alumina, such as caustic soda, the neutral point with litmus is reached, just when the whole of the sulphuric acid is combined with soda and the alumina precipitated. Thus:—

$$Al_2 3SO_4 + 6NaOH = 3Na_2SO_4 + Al_2O_3 + 3H_2O.$$

If soda be added in excess some of the alumina is dissolved to form sodium aluminate.

Substituting, say, lime as a base for caustic or carbonate of soda, we get the whole of the alumina precipitated until we come to the neutral point as before, but an excess of lime is incapable of dissolving, and therefore combining with the alumina. We then get a paper containing free bases, that is, basic to litmus.

The most ready means of testing paper is to get the three indicators, litmus, methyl orange, and congo red, and prepare perfectly neutral and very dilute solutions of each with recently boiled and rapidly cooled distilled water. A bottle of each of these is kept from contact with the atmosphere. A stirring rod is dipped, say, into the methyl orange, and a small bead from this allowed to fall upon the paper to be examined. At equal intervals drops of the same indicator are placed side by side so as to form a row of drops. The time that each drop has been in contact with the paper is known, and its rate of change can be noted by comparison with its neighbour. The rate at which the change takes place can be taken as a fair indication of its chemical condition. To guard against any disturbances due to impurities in the atmosphere, the strips of paper should be covered with watch glasses.

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A better way, perhaps, but one requiring more time, is to take equal weights of the papers under examination and place them, after tearing up, into equal volumes of a dilute solution of the indicator. This is best done in ordinary thin tumblers, and a piece of glass placed over each to prevent contamination with the atmosphere. After allowing to soak for three hours, the fragments of paper are pushed out of the liquid, and the change of colour of the solution noted against an equal volume of the standard solution under similar conditions.

The two above-mentioned methods are only qualitative, and may mislead us without other tests. Only those substances, whether acid or alkaline, that are soluble in water affect the indicator, so that we only get an idea of the soluble constituents.

The following is a ready method of determining the amount of basicity or acidity of the soluble constituents. Four grammes of the paper are placed in a beaker and digested with boiling distilled water. This is kept in an air bath to digest at about 140° Fahr. for three hours. The hot water is run off, and the paper twice digested with hot distilled water. Care should be taken that water is free from carbonic acid. To the aqueous extract is added a drop of neutral litmus, and the titration is performed with decinormal sulphuric acid, if the extract be basic, and if acid, with decinormal sodium carbonate. In the latter case the solution must be boiled to expel the carbonic acid, and if by any chance too much of the sodium carbonate has been added, the solution must be titrated back with $\frac{N}{10}$ H_2SO_4. The writer, after careful trials, abandoned the other two indicators, methyl orange and phenol-phthlein, as the presence of substances such as gelatine seemed to mask their true end reaction.

It is advisable always to express the chemical condition of the paper, whether it be acid or basic, in terms of sulphuric acid, in order that the results with both kinds of paper may be capable of comparisons.

It is most important to determine the chemical condition of the paper as to its insoluble constituents. This is not done with the same amount of accuracy as the soluble. It can be got at by determining the total constituents and the soluble constituents, and taking the difference as being the insoluble.

Supposing the paper, upon superficial examination, gives an alkaline reaction with litmus, and that the amount of alkalinity of the constituents is determined with litmus, a fresh quantity of paper is taken and digested with hot distilled water containing

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three times the quantity of acid required for the soluble constituents. It is twice exhausted with distilled water as before. To the extract is added litmus; it is then titrated back to the neutral tint with sodium carbonate. The difference between the two titrations gives us the alkalinity of the total bases. The risk that we run here is of some of the acid being condensed by the cellulose, and also the cellulose and starch being acted upon by the acid. The after-washings with distilled water, if carefully done, overcome the former, and we think that, in regard to the latter, very little action takes place if the temperature is kept at 130° Fahr. It is important, furthermore, in this case, to use only litmus as indicator.

The lecturer has pointed out the important part played by iron salts in the degradation of papers. Iron salts, like salts of alumina, are withdrawn from solution by the fibre. They both, we believe, readily undergo dissociation into acid and base in the fibre.

There is conclusive evidence of this in the case of iron salts, and it is extremely probable in the case of alumina. Both the bases formed, namely, ferric oxide and alumina, are insoluble, but the dissociated acid may enter into solution and be removed by washing, leaving the pulp basic. The iron base has the power of oxidising and weakening the fibre by abstracting oxygen from the atmosphere and giving it up to the fibre. It is probable that alumina has this power also, but in a much less degree. This action takes place most readily when the material is slightly moistened and exposed to the atmosphere.

The effects of iron and copper salts upon cellulose at higher temperatures can easily be illustrated, especially the former. An ordinary india-rubber stamp if moistened by pressing upon a pad impregnated with a solution containing one part of ferrous sulphate per 1,000 of water, and then pressed upon a sheet of paper, leaves no discoloration when the same is allowed to dry. If, however, the paper is placed at some distance from a flame, so as to allow it to get hot without charring, the device imprinted on the paper quickly develops up in sharp outline. The heat appears to disengage an almost infinitesimal quantity of ferric oxide, which, in its extremely finely divided state, acts as a conveyer of oxygen to the paper and chars it wherever the salt has been allowed to come in contact. The same experiment should be tried with a copper salt and with acetate of alumina.

The above experiments are convincing that the presence of such bases, when even in minute quantity, are liable to degrade

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papers considerably in hot climates. It appears also probable that in a very damp climate salts of these bases act as bearers of oxygen and in some cases the bases themselves.

The above-described methods for the determination of the basicity of a paper give no indication as to what bases are present. The iron salts are more liable to dissociation than the salts of alumina, and are more to be feared in large quantities on account of their destructive action.

The presence of such bases as these have an important influence upon a paper's qualities for taking different colouring matters. Many colouring matters form an insoluble lake with alumina; this in all probability adds to the fastness and permanence of the colour, but often considerably alters its shade from that of the original. Some aniline colours also will not stand the presence of bases, whilst others will not stand acid constituents.

A great deal of trouble is often experienced with printing inks and some kind of paper, which can be traced to these constituents, which, although present often in minute quantities only, are sometimes capable of exerting a very powerful and destructive influence.

I have seen it stated, in some cases, that chlorides are destructive when present even as a chemical residue in papers. I believe that some chlorides are, such as chlorides of alumina, and that their destructive action is due to dissociation, which takes place within the fibre, but I should hardly think that chloride of sodium, or common salt, is destructive, at least as a residue. This is a question, however, on which we have very little knowledge.

We will now deal with the potassium iodide test in its application to paper, and you will see, I think, if you follow my arguments, that any inferences and deductions can only be arrived at after a thorough knowledge of all the conditions and of the chemical changes that take place when the conditions are varied.

Mr. E. Hughes, in a paper on "Water as a Catalyst" (Phil. Mag. (v.), 35, 531-534), remarked that paper, when moistened with potassium iodide solution and exposed to the light, assumes a brownish-violet tint. As the staining varies very greatly with different kinds of paper, being greatest with highest glazed note-paper, he attributes it to the presence of chlorine in the paper. Hughes studied this reaction from the point of view of the moisture acting in some way as a promoter of chemical change. We desire to regard it solely from the point of view of the paper itself.

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There are several other explanations of this peculiar reaction which appear to be far more probable than that given above. The potassium iodide may contain potassium iodate, and free iodine may be liberated by the action of the alum contained in the paper in these substances. As paper almost invariably contains starch, we should expect to find that the colour produced was more of a deep blue, due to the action of the free iodine in the starch of the paper. If, however, paper containing starch be dipped into a weak iodine solution, so as to produce a deep blue colour, this, on exposure to bright sunlight, is very rapidly discharged. In this case there appears to be very little doubt that the iodine, in combination with the starch, is converted by the action of moisture contained in the paper into hydriodic acid, and that oxygen is liberated.

In the case of paper moistened with potassium iodide, the production of a colour seems rather to indicate that iodine is in some way liberated, but that it is not converted into visible hydriodic acid as the moisture is evaporated from the surface before there is time for this action to take place. Free iodine cannot be formed by the action of an acid upon potassium iodide unless it also contain iodate. It is possible that some iodate is formed by the oxidation of the atmosphere, and that if the paper is of an acid nature free iodine may then be liberated. Supposing this to be true, in what way would the character of the paper used affect this change? Hughes found that the stain produced is greatest with highly-glazed notepaper. It seems hardly probable that the explanation last given can account for the staining, since highly-glazed notepaper is about the least likely to give an acid reaction. There are good grounds for this statement. For many months the lecturer examined daily about ten samples of writing paper quantitatively for chemical condition, of which a record was kept, together with particulars of chemicals added to furnish. Out of the whole lot of papers examined there is not a single instance of paper containing free acid. Although many of the papers gave an acid reaction to litmus, none were acid to methyl orange, showing that the alum is always in a basic condition. Many of them are alkaline even to litmus, especially those which are tub-sized only and made in districts where the water is hard.

I am doubtful whether alum alone would [illegible] it might do, the conditions being peculiar. [illegible] being most liable to staining under these [illegible] imply quite a different cause than that given [illegible]

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of this description, when moistened with potassium-iodide solution, it appears that the air in contact with the paper would have its maximum effect, since most of the solution is on the outside of the paper, as it were. With a soft paper, the solution would be absorbed more into its body, and if the alum promoted this change, we should expect it to do so more rapidly in the latter. If, on the other hand, we assume that chlorine in the paper is the cause, we would expect the latter to be more stained, since it is more thoroughly permeated by the liquid. It is impossible, in my opinion, for chlorine or hypochlorites to be present in the paper, as they are quickly oxidised by the atmosphere; nor is it possible for the chlorine present in the paper, in the form of chloride, to liberate the iodine from potassium iodide.

Although it cannot at present be proved, the only explanation of this staining appears to me to be as follows:—The atmosphere contains both ozone and hydrogen peroxide, both of which have the power of liberating iodine from a solution of potassium iodide. So long as moisture is present this liberation can be effected, and is probably greatly accentuated when using paper as a medium. The action is greater in the light, as those substances are more abundant in the light. The iodine so liberated may enter into combination with the starch, and when the paper is dry no further action takes place. This appears at first sight not to agree with the statement that the iodine-starch colour is discharged on placing the paper in bright sunlight. But I think there is no difficulty in explaining this on the same assumption. Ozone may complete the change. It probably takes place according to the following equation:—

$$I_2 + H_2O = 2HI + O$$

Ozone may promote the change by the withdrawal of oxygen from the water, converting the ozone into common oxygen—

$$O_3 + O = 2O_2$$

As a proof that this change does not depend upon the composition of the paper itself or anything contained in the paper, starch alone, after treating with iodine to produce this blue colour, fades similarly under the action of bright sunlight.

Iodine has been used in paper as potassium iodide, together with starch, as a means of estimating the amount of ozone in the atmosphere, by noting the amount of colour produced for a given time of exposure. It has proved itself to be altogether unreliable, as might well be inferred from what has been above stated. The presence of nitric acid in the air also tends to

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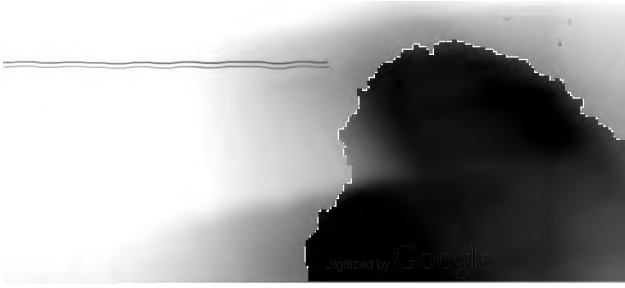
produce this discoloration. We must, therefore, regard it as being a very mixed reaction.

Paper containing starch and immersed in a dilute solution of iodine changes to a blue colour in proportion to the amount of starch present. If this paper be half immersed in the solution, it will be found that that portion still kept damp, but exposed to the air, loses its colour much more readily than the immersed portion. In fact, the latter does not become white again until the solution has lost its free iodine by contact with the atmosphere.

Some of the questions raised in this lecture are rather abstruse, at any rate for the ordinary student, but they are worthy of careful consideration by the paper mill chemist. I can hardly expect many to assimilate all that is here set forth. I have given it partly because it should prove of some value to those who have to prepare papers for special purposes, such as drawing and perhaps photograph papers, and such papers that have to stand some of our fugitive inks. I have, however, another object in bringing this matter forward, and that is to show those who are in the habit of applying rough-and-ready tests to papers and drawing hasty conclusions that a little knowledge is dangerous. And I do this not without some reason, because cases have come under my notice more than once of absurd tests having been applied, and still more absurd conditions having been imposed, in contracts which are thought to be a safeguard as to composition of paper, but in effect prove to be vexatious impositions and devoid of all reason. If those stationers and printers who wish to make conditions in their contracts for the purpose of safeguarding themselves against any chemical residues which might prove harmful either to the paper itself or to the inks used upon it would consult some authority who has made a study of the subject, both from the maker's and the printer's point of view, some satisfactory and practical test might be devised, which, besides being effective, might in no way prove vexatious to either party.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LECTURE VIII.

THE FUNCTION OF WATER IN THE FORMATION OF A WEB OF PAPER.

Effects of water on fibres—Flexibility—Felting qualities—Elasticity—Shrinkage on drying—Removal of water—Influence of temperature when hydraulic pressing—Capillarity—Brittleness—Effects of rosin—Beating—Calendering—Physical properties of fibres.

In a previous lecture an attempt has been made to show that water has a very important duty to perform in the felting of fibres for the production of a sheet of paper. An early writer, who described paper as being an aqueous deposit of a fibre, gave a somewhat inadequate definition, and only partially revealed its real nature. It would be better perhaps, and for reasons that will be more evident when the real functions of water are correctly stated, to define paper as an aqueous deposit of any *vegetable* fibre. As far, at any rate, as this lecture is concerned, we will accept this definition, as my remarks can only be said to apply to paper of vegetable origin.

When an ordinary waterleaf is wetted, it not only expands, but becomes also very much weakened, so that it will often fall to pieces when held between the fingers. This change in strength that paper undergoes on assimilation of water is the result of the action of the water upon the ultimate fibres of which the paper is composed, and it will be necessary to investigate this very carefully in order that we may understand the chief part that water plays in its formation.

I shall endeavour to show that the effect of water upon cellulose fibres is to give them increased flexibility, which allows of the fibres being drawn apart with comparative ease when

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unsized waterleafed paper is wetted. Conversely, in the production of paper, the fibres at the start exhibit their greatest flexibility and pliability as they are suspended in a watery medium. In the process of the formation of the web they are first of all deposited so as to interlace one with the other, and, in course of treatment, become more stubborn and resistant by the removal of water until, when air-dry, the paper has gained its maximum strength.

It is, so far as I know, impossible to examine the ultimate fibres, say, of cotton, linen, or of wood, for varying degrees of flexibility under the influence of moisture, but it is possible to obtain a mass of amorphous cellulose, we have every reason to believe, closely allied in general physical properties to that which constitutes the cell-wall of the ultimate fibres, and from the physical behaviour of such amorphous cellulose the general deportment of fibres under similar treatment may be inferred.

Sheets of amorphous cellulose, possessing in the aggregate the properties of the cotton fibre, may be obtained by heating down to dryness on a glass plate a solution of cellulose thiocarbonate. After washing, a flexible sheet of cellulose is obtained which can be examined for flexibility under varying conditions of moisture. The film itself varies in properties according to its mode of preparation. This fact seems to indicate that ultimate fibres vary in the same way according to their mode of elaboration. The property which concerns us most is that of flexibility, and this can be made to vary at will by altering the conditions of setting the cellulose from its compounds in solution. From this "elastic" property of cellulose the difference in the elasticity of various ultimate vegetable fibres may be inferred by which an explanation is afforded of their great differences in felting power.

Cellulose films may be obtained as above described that are tough and rigid when in a dry atmosphere; but when placed in a damp atmosphere they become remarkably flexible, and on immersion in water possess the pliability of a sheet of rubber. Films, on the other hand, may be obtained, by altering the conditions of preparation, that exhibit only a slightly increased flexibility on exposure to a damp atmosphere or immersion in water. A film may also be obtained that when dry is extremely brittle, so much so that it will fly to pieces spontaneously, or when slightly scratched on the surface. It is cellulose of this nature that exhibits the greatest range of flexibility when acted on by moisture. It appears from the study of amorphous cellulose towards absorption in water that the particles have,

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as it were, a certain elasticity, and the removal of water by heat causes the particles to come close together, and that whilst in close contact, due to the removal of water by heat and such means, the particles are in a state of tension. This appears to account for the brittle nature of the material when the water is removed by heat. When this is brought in contact with water it expands to a certain degree, taking up water and recovering its elasticity. It appears, then, that the greater the tension in the dry substance the greater its affinity for water, and hence the most brittle substance when dry is most pliable when wet.

If the water be removed from the substance by compression in the first instance, the particles are brought permanently into close contact, and being free from tension they have no desire to take up water. The material partakes of this nature in proportion to the compression. Material so prepared is tough and rigid when dry, and preserves this property in a measure when wetted. It neither expands nor assimilates moisture when wetted to anything like the degree of the former preparation. The cell-wall of an ultimate fibre consists of cellulose which is more closely allied to one or other of the above, according to the conditions of its elaboration. Some fibres, it will be noticed, produce a very strong paper, which shrinks enormously on drying. The strength of a paper cannot, however, be taken as a measure of the felting properties of the constituent fibres, as the length of the fibres has a lot to do with the strength of the paper. A small amount of moisture is often sufficient to materially affect the strength. Paper, when put in a testing machine, and under a moderate amount of strain, easily breaks asunder if the finger is moistened and drawn across it. The strength is materially lessened even by breathing on the surface when under strain.

We see then that it is altogether a mistake to assume that water acts merely as a medium in which the fibres are suspended. The fibres expand by taking up water, and the amount that they take up is dependent upon the moistness of their surroundings. Their flexibility is in proportion to their expansion, and therefore to the amount of water present.

In the form of pulp the fibres contain their maximum of water, and therefore exhibit their maximum flexibility. The first part of the water is removed by gravitation; this cannot affect the flexibility of the fibres. The next portion of water is removed by pressure; this is probably insufficient to affect the flexibility, but makes the web somewhat stronger by causing the fibres to lay closer. The water removed by these two processes is the surplus

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water in which the fibres have been suspended. The amount of water really assimilated by the fibres themselves, by which their volume is augmented, is relatively only a very small quantity of that used in the pulp, probably only about one-fortieth and sometimes very much less. The fibres, on immersion, in some cases may expand to double their dry volume. In doing so, they would absorb about three-fourths their weight of water. The web, after passing the second press-rolls, contains on an average about four times its weight of water, or more than five times the water necessary for the hydration of the cellulose. As the web passes on to the drying cylinders the surplus water passes off, first being converted into steam. As this goes on, the cellulose becomes dehydrated by giving up its water. This appears at first as sensible moisture, merely separating from the cellulose; it, however, quickly becomes vaporised by the heat, but produces the sense of dampness to the web so long as it is being emitted.

Here we touch upon another question, namely, that of the effect of water of different temperatures upon the flexibility and expansion of cellulose. This question has an important bearing upon that of the stuff working "wet" or "free" on the machine, also one closely allied to this—the removal of water from paper stock by hydraulic pressure. We have to appeal again to the properties of amorphous cellulose sheets or blocks under similar conditions. Supposing we put into cold water a mass of the cellulose material beforementioned that has been previously dried by heat, and wait till it has taken up as much water as it will, we weigh it and find it has doubled in weight. If we then put it into warm water and allow it to remain for some time, it will contract and be found to weigh less. It will weigh less and contract more the higher the temperature of the water. There is every reason to believe that ultimate fibres behave in a similar way. In hydraulic pressing paper stock with well-beaten rag stuff by the application of 300 lbs. per square inch for the production of cakes 15 inches in diameter by 5 inches deep, if cold water be used the moisture after pressing contains about 50 per cent. of water and 50 per cent. of air-dry fibre. It is well known that it requires a very great increase of pressure to obtain a mixture perceptibly drier than this. It appears that this amount of water is fairly bound by the fibre itself. Supposing, now, that the paper pulp is pressed whilst very hot, the water is found to drain away with much greater ease, and a moisture is easily obtained containing 40 per cent. water and 60 per cent.

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air-dry fibre. Notice this confirms my former statement, namely, that fibres absorb about three-fourths their weight of water, which is taken up by the cell-wall and gives the fibres their increased bulk and flexibility on immersion. I would put it this way: the fibres in a watery medium take up 100 per cent. in the cold or 67 per cent. when the liquid is hot. This affords an explanation of the difference in the behaviour of stuff on the machine when heated. Also it helps to explain why heat tends to make "wet" stuff work free, and it merely comes to this—heat tends to dehydrate cellulose.

This difference cannot be due to the expansion of the water as water; there is only a difference of 5 per cent. between cold and boiling water; this would only make a difference of 2 per cent. in the composition of the pressed mass. The only true explanation appears to be that the fibres contract in the hot water, and therefore retain a less quantity of water than when cold.

The cellulose is converted into cellulose hydrate by beating. The hydrate is higher when the beating is prolonged. On raising the temperature of the stuff the cellulose is dehydrated, and the extent to which it is dehydrated is dependent upon the temperature through which it is raised. The surplus water that is not in chemical union as hydrate is easily removed by pressure; greater pressure is required to dehydrate. It follows, then, that on a paper machine, only that portion of the water that is not combined with the cellulose is removed by pressure, the combined water being removed by heat in the drying cylinders.

With regard to the working of the stuff on the endless wire of the paper machine, the problem is very much more complex. The contraction of the fibres *per se* cannot account for the readiness with which the water leaves the wire. The difference in the temperature is only a matter of 40° Fahr. at the outside, and the water retained in either case is tenfold that assimilated by the fibre itself. It appears rather that what is known as the capillarity of the fibre is decreased. By capillarity is meant the power of taking up a liquid as a wick soaks up oil. The decreased volume of the fibre is accompanied by a decreased power of soaking up the liquid, it therefore runs off, like water off a duck's back, having less affinity. Bodies of the nature of alkali retain surplus water in proportion as they become softened and hydrated by the assimilation of water. Nitro-celluloses, such as gun-cotton, retain little water after draining; this is largely due to the fact that their fibres are rigid, and have lost that pliability by which

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the small fibres are enabled to seal up the small holes which allow of the escape of water.

As the fibres are rendered more rigid and inflexible by the increase in temperature of the water medium, they lay one upon the other in the web, more like a number of sticks or bavins than a mass of flexible fibres.

It is easy to see that such a mass would allow of the escape of water with much greater freedom. This, probably, is of valuable aid to us in manipulating the stuff on the "wet-end" of the machine. By regulating the temperature, the stuff may be made to work "free" or "wet" at will.

We next come to consider why the stuff is caused to work wet by being left long in the chest or in the engine. The effect of water upon cellulose is far from being instantaneous. The cellulose composing the cell-wall of a fibre cannot be regarded as being uniform in constitution. It consists of an exterior that is much more resistant to all sorts of chemical attack than the interior. If the unbroken ultimate fibres be suspended in water, their softening and expansion is much more gradual than if the same had been cut into several pieces by the action of the beater roll. In the latter case, all parts of the fibre are exposed to the action of the water. This appears to account for stuff working very wet when kept long in the beater. If kept very long in the chest, the long-continued action of the water penetrates the outer covering, and more thoroughly expands and softens the fibre.

When paper is hard-dried by exposure to a temperature of 220° Fahr., which is sufficient to drive off all the hygroscopic moisture, it often is found to be quite brittle. This is probably due to the fact that the cellulose composing the cell-wall of the fibres is in a state of tension, due to the removal of water; as with the film of amorphous cellulose the strength is restored when it regains moisture, unless the qualities of the cellulose are permanently impaired by oxidation at this temperature.

The surface of a glazed paper is soon removed by moistening. This is due to the expansion of the fibres. When the fibres are dry, although often brittle, they partake somewhat of the nature of metal, and admit of a bright polished surface by the application of pressure or friction. On wetting, the fibres first of all regain a certain amount of elasticity which they had lost when very dry. They stand up and come apart to a certain extent, and undo the effects of the pressure. Paper can be smoothed on its surface, but not highly glazed when damp, for this reason; also paper, on

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account of its brittleness when very dry, is much more likely to be crushed under the action of the glazing rolls.

With rosin-sized papers, the ease with which they part, when re-wetted, is no measure of the pliability of the fibres, as they are cemented together with rosin, which is not affected by the water. The cementing by the rosin is done as the paper passes over the drying cylinders. The re-wetted paper, therefore, is much stronger than the paper with the same degree of moisture before the same has passed over the drying cylinders.

We have already seen that dry amorphous cellulose may so be prepared as to fly to pieces when the surface is merely scratched. When this is brought into contact with water, it expands to a certain degree, taking up water, and recovers its elasticity, and is no longer brittle. If, however, the moisture is removed by forcing the particles together under high pressures, the cellulose is not brittle and expands less on immersion. It appears probable that similar stresses are set up in the ultimate fibre, and that these vary according to the conditions under which the cellulose has been elaborated in the living plant. These are stresses set up when the cell is deprived of moisture, and only relieved when the moisture is allowed to re-enter. In the case of an amorphous film of cellulose, prepared so that it is capable of considerable expansion when wetted, the water appears to enter into some sort of chemical union with the cellulose, or to be dissolved or solidified by it. The hygroscopic moisture appears to bear some direct relationship with the absorption of water on immersion. That water is essential to these changes is apparent when we use any other liquid. We are all surprised to find, for instance, that paper retains its dry feel when immersed in very strong alcohol. It also retains its strength, as there is no water present to produce any flexibility of the fibres. It is possible that the firmness of a paper is actually increased under absolute alcohol, as the liquid has the power of withdrawing even the hygroscopic moisture of the paper, just as though it had been placed in an air-bath. The behaviour of vegetable fibres suspended in a medium of strong alcohol demonstrates that they have lost their felting power. Other liquids may be used, such as ether or carbon bisulphide, with similar results. The felting power of the fibres in presence of water is not then due to the fact that they are in presence of an inert liquid medium, but that they are suspended in a medium which has a powerful influence upon their physical and chemical constitution. The only liquid, as far as I am aware, that could exercise this influence is water.

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The question as to whether fibres stick together on drying in contact is worthy of consideration. Is it possible that there can be some substance of a glutinous nature affected by water that causes the fibres to adhere when dry? I think there is every reason to believe that no such substance can exist. If such substance existed, it would probably be capable of separation from the cellulose of the fibre. From the manner in which dry paper tears, it appears rather that the interlacing of the fibres is responsible for the strength, than that it can be due to any glutinous materials.

The views above expressed as to the function of water in the formation of a web of paper agree closely with what is noticed in practice. Fibres which have a tendency to work "wet" are generally those which have the greatest shrinkage, and result in the production of the strongest papers.

The effect of long beating or long standing in the chest is to produce wet stuff with an increased shrinkage in the web. Heat applied to the stuff before passing on to the wire tends to make the stuff work "free." The shrinkage in the web is found to be greater when the stuff has laid for a long time in the chest, as on Monday morning.

For the production of very strong papers, such as "banks," it is customary to leave the stuff for a long time in the engine. One object of this is to brush the stuff out, so as to leave the fibres intact. The effect that it also has, however, is to cause the stuff to work wet by the increased assimilation of water by the fibres, which results in their increased flexibility.

The paper produced is better felted, it has a greater shrinkage, and is stronger.

Many fibres after bleaching are condemned, entirely on account of the stuff working too wet to be run on the machine. In the case of one fibre which I found to work very "wet," I obtained a sheet which showed a shrinkage of 30 per cent. in one direction on drying. The paper obtained was exceedingly hard and tough, but, in spite of the good qualities of the paper produced, the raw material was condemned as being impossible to run over the machine at a sufficient rate to make it pay.

The condition of a fibre in this respect is largely dependent upon the way it is beaten. Beating has become quite a fine art, also the construction of beaters suitable for the production of stuff adapted to any specific purpose. Some years ago it was thought that a certain paper possessing certain qualifications would have to be made from certain raw materials. It is now

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becoming widely recognised that the manipulation of the stuff in the beating and in the other mechanical processes is an ever-increasing factor. Wood may be made to partake somewhat of the nature of cotton, and cotton, in a less measure, perhaps, of the nature of wood. Wood may also be made to replace either linen, for the manufacture of strong banks, or it may be made soft and spongy suitable for illustrated papers and litho work. It must not be forgotten, however, that the chemical treatment preparatory to the beating has a wonderful influence upon the condition of the fibres; but this, again, leaves the fibres with more or less affinity for water.

It stands to reason that it is more difficult to make a short fibre partake of the nature of a long fibre than a long fibre that of a short fibre. You cannot make a fibre longer, but you can always make it shorter by beating. A fibre that has a tendency to work free can be treated in such a way as to cause it to work wet. *Vice versâ*, a fibre that has a natural tendency to work wet can be so treated as to cause it to work comparatively free. A long fibre can also be so treated as to possess some of the characteristics of a short fibre. It may be flattened by the action of the beater-roll or bruised or cut sharply.

It has been above-stated that amorphous cellulose fibres, when subjected to high pressure for the removal of water, are toughened and do not exhibit the same affinity for water as when the same are dried by heat.

When papers are calendered they lose some weight, which, I believe, is generally acknowledged not to be restored on exposure to air. It appears, therefore, that pressure is responsible for this by bringing the particles more closely into contact. A film of amorphous cellulose differs from a sheet of paper, in that the former is homogeneous in structure, whilst the latter is composed of a mass or network of fibres. It does not follow that pressure will add to the strength of paper, as when carried to excess it may so affect the fibres as to reduce their felting power. In this respect, then, the two appear to differ.

If rigidity is obtained by the removal of water by heat, it results often in the production of a more or less brittle paper.

Hygroscopic moisture is that moisture that a fibre retains when allowed to dry in an ordinary atmosphere. When wood retains 10 per cent., cotton and linen will be found to retain about 7 per cent. The figures in a measure represent, we believe, other things being equal, the relative flexibilities of these fibres

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and their relative powers of shrinkage; but this wants further confirmation, as there is by no means sufficient data to go upon.

The chief function of water in the production of a sheet of paper is to render the fibres which are suspended in it as a medium flexible and expanded. By the gradual removal of water, which results in the production of inflexible fibres, we see that the paper is formed.

The subordinate function of water is to provide a medium in which the fibres are first of all unravelled and often disintegrated. The medium also enables the fibres to be held in suspension and introduced in a suitable form to the wire of the paper machine. This suspension of the fibres also allows of the free action of the shake of the machine, which causes the fibres to interlace and build up one upon the other.

The first action is primary, and the second entirely subordinate; as no other fluid would so act on the cellulose as to render it flexible and capable of felting, no other liquid medium could be made to answer the purpose.

We have seen how this action of water upon cellulose throws light upon the working of various fibres on the machine, and the behaviour of paper under the influence of moisture. We have seen, also, how the abstraction of moisture affects the properties of paper, and how the affinity of paper for water on immersion may be explained. It affords also an explanation of what is known as working "free" or working "wet," and of the changes of beaten stuff in this respect after long keeping. It appears to point to the possibility of largely modifying the physical properties of any one class of fibre to produce a range of papers that could be only otherwise produced by using different raw materials. It appears probable, also, when supplies run short, or for other economic reasons, that one class of fibres may, within certain limits, be supplied by another. Much is already being done in this direction, and the same has been aided largely by improvements in the art of beating and in chemical treatment. In my humble opinion, one great problem of the future will be, not the discovery or the utilisation of special fibrous raw materials for the production of papers for which they are considered specially adapted, but, given certain cheap and abundant supplies of raw material, how best to treat and modify the material, both mechanically and chemically, so as to adapt it to as many classes as possible. The processes must be both cheap and effective, and no great progress can be expected without the aid of the strictest scientific methods. The physical properties of the material should

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be carefully studied, because, after all, the difference between one paper and another is chiefly a physical difference, which can be largely wrought by mechanical means. I think it must be admitted that one great study in this connection is that of the behaviour of cellulose towards water, which has such a powerful modifying effect upon its physical properties. The action that water has upon cellulose is largely influenced by the mechanical treatment that the cellulose receives when in contact with water.

It appears, therefore, that the problems of the future will be as much mechanical as chemical, and that we must accept the inevitable by abandoning one class of raw material in favour of a cheaper, if it is by mechanical or chemical means capable of replacing the same and fulfilling a like purpose.

REFERENCES.—The foregoing lecture is largely abstracted from a series of articles upon "The Function of Water in the Formation of a Web of Paper," scattered over several numbers of the PAPER-MAKER, but now out of print. For a more scientific explanation of the hydration of cellulose see the various publications of Cross and Bevan, also my own communications to the CHEMICAL NEWS and the JOURNAL OF THE FRANKLIN INSTITUTE.

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LECTURE IX.

*THE PERMANENCE OF PAPER.

The permanence of paper—The cause of deterioration—Early attempts at preservation—The effects of the fibre—Sizing—Clay—The atmosphere—Sunshine—Temperature and moisture—Discoloration—Fading of water colours—Organisms—Moisture—Fermentation—Nitrogenous matter—Methods of examination for—Liability to decay.

THERE are two sets of causes to which the destruction of papers are chiefly due: destruction by minute organisms and insects, and destruction by deterioration, due chiefly to oxidation. The former may be considered as purely physiological and the latter as purely chemical. The public of the present day care little about the permanence of a paper; in fact, there is no reason for them to care, as far as the greater part of our literature is concerned. With the ancients it was quite different; their paper was exceedingly costly, and was frequently used for the preservation of valuable records that were kept for centuries without destruction. They made a close study of the permanence of papers.

According to Pliny, they used to preserve their paper and books from moths by washing them over with cedar or citron oil. The oil gave to the books an agreeable scent, and they were known as *libri cedrati*. Pliny attributes the preservation of the books found in the grave of Numa solely to this precaution. He states that a certain writer named Terentius, when digging a piece of land on Mount Janiculum, found in a stone box the book of Numa, written on Egyptian paper (papyrus), which was quite preserved, in spite of the fact that it had been buried 350 years in the earth, because it had been steeped in oil of cedar. Koops says that there were found, according to Count Caylus, sometimes in the boxes containing Egyptian mummies, very neat

* The first portion of this lecture, dealing with the early methods of preserving papers, was communicated in substance to the columns of PAPER AND PULP, but now out of print.

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characters written on linen. Koops imagines that the linen must have been dipped in size or gum, or the ink would have blotted. I mention this, as I believe that the early use of size, or something which the size contained, played an important part in the preservation of papers, and fabrics which were once made to answer the requirements of paper. In consequence of the liability of linen to become mouldy, skins were used as a writing material.

The Royal Society of Sciences, at Gottingen, in 1773, offered a premium to anybody who could answer the following questions: How many insects are found that are detrimental to records and books? Which of the materials, as pap, glue, leather, wood, thread, paper, &c., are attacked by each kind? And which is the best and most approved remedy, either to preserve records and books against insects, or to destroy the insects? Dr. Herman, of Strasburg, obtained the premium.

There were five insects that were proven to be truly destructive. There were nine insects that are generally credited with doing harm that were proved to be without mischief. There were six that appeared doubtful; among them may be mentioned the book-louse or paper-louse. To preserve the books against insects and to destroy the latter, there were many recommendations. Among the most important of them, as far as we are concerned, is to recommend the bookbinder to use glue mixed with alum in place of paste.

Koops tells us that the paper of his time in North America was speedily destroyed by dampness and insects. In consequence of this, Mr. Francis, of Neufchatel, induced the Society of Sciences, of Philadephia, in 1785, to offer a premium for the best answer on the following question:—

Is there an effectual remedy to protect paper against insects?

The Society also offered another premium of 25 moidores for the best method of making paper for St. Domingo which would resist insects, and requested to have samples to prove its quality. Several answers and samples were received, but all, so Koops tells us, recommended to mix the size or sizing agent with sharp and bitter or other ingredients which might kill the insects. Among the substances mentioned we find vinegar, alum, vitriol, salt, turpentine, extract of aloes, tobacco, wormwood, camphor, and arsenic. The use of vitriol would, undoubtedly, be absurd, on account of its action upon the paper. Arsenic is a good germicide, but might be found objectionable on account of its poisonous character. The one substance that appears to have been used from the earliest ages up to the present time is alum.

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Alum at the present time is found to be a very necessary ingredient of paper, but its powers of preservation have been in a large measure lost sight of.

Koops tells us "to prepare paper for preservation against insects, is likewise an object to which some of the proprietors of the new manufactory now building at Millbank have paid particular attention; and they flatter themselves they will likewise be able to bring to sale, and to lay before the examination of scientific men and the public at large, paper, in this view much superior to any heretofore manufactured."

It is a great pity that these questions have, since the beginning of the last century, been almost entirely neglected.

It is only within the last few years that Germany has, through its Government Testing Station at Berlin, shown to the world the importance of looking more to the future. The public are now slowly beginning to consider whether a paper has durability or not. Public opinion seems to have retrograded since the introduction of cheap paper, and is at last making an effort to reconsider those questions to which so much careful attention was paid during the latter half of the eighteenth century.

In this lecture we are considering the permanence, or rather the want of permanence, in papers, largely from the point of view of destruction by living organisms, but with the assistance of outside agencies. It is necessary that we should fully appreciate the conditions under which organisms are capable of flourishing and exercising destructive influences upon paper.

Durability of paper is dependent upon many factors. These might conveniently be summed up as follows:—

A. The paper itself.
B. The atmosphere.
C. The sunshine.
D. The temperature and moisture.

Under A we have (1) Fibre.
(2) Sizing material.
(3) Clay.

Under B we have the question of oxidation brought about by free exposure to the air. This is most intense when the sheets are fully exposed and hung up, and the liability to destruction is greatest in an atmosphere such as that of London, where the impurities from combustion, &c., exercise a destructive influence.

The action is very much reduced when the paper is stored in the form of reams, or when it is contained in libraries, &c., where the air can get at it very little, but, nevertheless, paper even in

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the leaves of books shut up in libraries is perpetually in contact with air, although the air has not free access. Under such conditions the action of the air is reduced to a minimum, and the action of light or sunshine is practically nil, except on the edges, and to a distance of about one inch inwards.

Paper is less acted upon in air when it is used for purposes of illustration and covered over with glass. Under such conditions the light which gets to it has a greater influence than the air.

As regards C, the sunshine has little or no effect when the paper is stored away. Under sunshine we would include any light other than artificial illumination, as all the light which reaches us emanates from the sun. There is a certain amount of action even in an ordinary room when diffused light alone is allowed to enter, but the effect of light is much intensified when the paper is exposed directly to sunshine, especially in summer time, no matter whether the sunlight traverses a glass window or not. Paper such as common "news," if left in the sun for some days, will have become discoloured, and will in fact have undergone as much change as a paper would if left in a dark place for one year. *Qua* light, artificial lights such as gas, candle light, and electric light have much less effect than sunlight, either direct or diffused, but, of course, gas is highly objectionable where permanent records are stored, on account of the products of combustion being destructive. It should be remembered, that the kind of light which destroys papers is just that kind which must affect a photographic plate, and consequently those sources of light are the most active which contain the greatest amount of actinic or chemical rays. Sunlight is far more active than the rest for this very reason.

The question of fading is distinct from, although closely allied to, the question of deterioration of paper. I would define fading as being a change, not in the paper itself, but in the material used to colour the paper. As the fading of a paper may result in a deterioration, at any rate, from a commercial point of view, the question may very well be considered here. As far as I am aware, there is no publication presented to the paper trade dealing with this aspect of the subject, but, nevertheless, it has been most carefully investigated from the point of view of the permanency of colours used for water-colour drawings. Such work, however, does not cover the whole of the ground, because water-colours are only superficially applied to the paper after manufacture, whereas ordinary papers are coloured in the course

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of manufacture, and the colour, whether pigment or dye, is disseminated through the body of the paper. Moreover, there is another distinction—water colours are only used on papers of a particular class, and prepared especially for the purpose—*i.e.* drawing papers; whereas most tinted and coloured papers, especially those of very pronounced and brilliant colours, are generally made of common and cheap materials. In our consideration of this matter we will exclude enamelled papers.

The researches conducted by Captain Abney and Dr. Russell throw light on the whole subject, and their conclusions should prove instructive to papermakers and stationers, as the conditions which affect the fading of water colours apply also, and in a like degree, to the fading of tinted papers, and it will readily be seen that the kind of light which is most destructive and the conditions which give rise to the most rapid discharge of colour are such as also affect the fibre to the greatest extent. It therefore very often happens that when a tinted paper fades, not only is the colour discharged, but the fibre is at the same time disintegrated, discoloured, and destroyed, and the paper instead of merely losing its colour and showing a white background, especially in the case of mechanical wood, gives rise, when acted upon, to a brown and dirty coloration.

* "But another point, and a very important point for the critics to take hold of, is this. It is all very well to say that light alone causes fading, but how about light and heat together? Would not the heat aid the light? This possible criticism was combated, I hope, in a successful way. A certain series of pigments, washed on paper, were taken and exposed on a vessel containing boiling water; similar papers were exposed to the sunlight free, that is to say, without the presence of boiling water. In some cases the fading was rather more rapid, in others less, and you will readily see why in some cases it was rather less rapid. You require moisture *plus* air in order to cause fading, and if you heat paper, of course you take away part of the moisture, one of the agencies which are conducive to fading. But the difference between those exposed on boiling water and those exposed without was so small that you might take the action of light plus heat as equivalent to the action of light alone."

We must conclude, therefore, from this series, that heat does not promote or accelerate the fading of colours in paper. In

* The above quotations are from Cantor Lectures before the Society of Arts on Light and Colour, delivered in 1888, by Captain Abney, F.R.S.

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order to ascertain what kind of light had the most effect, the authors exposed papers coated with different pigments under coloured glasses, so as to shut off different portions of light. It was found that under the red and green glasses the fading of the few pigments that succumbed was so small that it required a practised eye to distinguish it, but under blue glass the fading was almost identical with the fading under white glass. Now the red waves of light are the longest and the blue waves are the shortest, therefore it is the waves of light of the quickest oscillation which bring about the fading. It was furthermore found that every pigment (with a few exceptions which we need not trouble ourselves about) is permanent when exposed to light *in vacuo*. This indicates that light alone without the presence of air and moisture will not fade papers. It was furthermore found that when a paper is tinted with two colours one of which is fast and the other is fugitive, the fugitive colour is destroyed, and the fast colour is left unimpaired by exposure to light. It was established that moisture and oxygen were essential for the fading of colours in paper; the question remained whether they would fade without light. A stream of oxygen was passed through a tube containing some papers coated with pigments. Half of each paper was damped and the other half left dry. When this was connected with an ozone generator, "a great many are bleached entirely, thus proving, if you have ozone and moisture together, you get a bleaching without the presence of light at all." This action is very rapid. These are conditions that prevail at seaside places. "We come then to the conclusion that oxygen and moisture are sufficient for the fading of water-colour pigments, and that it is not absolutely necessary that there should be light present in order that this fading may take place." It will readily be seen that the conditions here favouring the fading of colours are on all fours with the conditions which are found to bring about the destruction of the fibre itself. Erfurt's book on the dyeing of paper pulp does not deal with this aspect of the subject.

Then apart from the above, we have the question D or temperature and moisture. As previously explained, when paper contains sizing material in a moist atmosphere and within certain limits of temperature, the deterioration or destruction of the sizing material is extremely rapid. If, however, the temperature is fairly high, *i.e.*, high enough to prevent the growth of organisms, the deterioration of the paper itself would not be so rapid, although the gelatine size would undoubtedly be destroyed.

When paper is totally immersed in water the fibres are not

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so liable to decay as when the paper is hung up or exposed to the atmosphere charged with moisture. These various details will be considered more particularly further on.

There are other conditions which will affect the permanence of papers. We can take an extreme case such as ordinary soil. Even a pure cellulose paper when buried in the ground or covered over with ordinary earth will be completely disintegrated, and even dissolve away in a very short period of time, due to the "humic" and "ulmic" substances contained in the soil, which have a rapid solvent effect even upon pure cellulose.

We will now consider paper as a medium for the cultivation and growth of bacteria and minute organisms, because by so doing we shall be better able to form a mental grasp of the conditions which favour the growth of these organisms, in the course of which they bring about the destruction of the paper.

It may be taken generally that any organism which is capable of development or cultivation on gelatine is also capable of development on all papers that contain animal size. Furthermore, all those organisms, moulds, yeasts, &c., which are capable of developing and acting on starch in one or other of its forms, are also capable of developing and growing in papers which have been sized with starch, provided, of course, that such papers are exposed under such conditions as will favour the growth of these organisms. Rosin size, however, is not affected by organisms, but on the other hand it is the most susceptible of all the sizing materials to the action of light.

Some years ago I made use of a process called the "fermentation process," which was used for the destruction of gelatine and starch, and other sizing materials used in papers, before the papers were reduced to pulp. The process was an extremely simple one. Papers were taken in bags or bales and immersed in water for a few minutes so as to thoroughly wet them through. These bales were then placed in a damp place, not too cold or too hot, and allowed to remain in the bales in a damp condition, or placed in tubs, and were kept away from exposure to the atmosphere and in the dark. After a time a change took place in the appearance of the papers. They developed a musty smell. They also developed brilliant spots, red and blue and different colours, showing the formation and development of organisms producing pigments.

These organisms preyed upon the sizing material and destroyed it, some of them converting the size into colouring matter, whilst other organisms known as the liquefying organisms,

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broke down the gelatine and destroyed its gelatinising properties altogether and rendered it soluble.

After this treatment had been allowed to develop to the extent of destroying the sizing material, and before it had any chance of acting on the cellulose itself, the papers were pulped in the usual way, and the fermentation process could be arrested entirely in the process of pulping by the addition of a small quantity of antiseptic, which entirely destroyed the organism.

It may interest you to know what the organisms are which are capable of acting in this way upon the nitrogenous and farinaceous matters contained in papers. I will give you some idea of a few of them:—

There is *Saccharomyces nigia*, which forms a black crust on the surface of gelatine.

The *Bacterium indicum* produces a brilliant red coloration.

There is *Saccharomyces rosaceous*, which produces a pink colour.

On certain forms of starch the *Bacterium prodigiosum* produces a cloudy red growth, which gradually acquires a brownish colour, and in doing so it breaks down the starch.

A very common form of mould, the *Penicillium glaucum*, produces a greyish spot on the surface of starch.

Mr. C. F. Cross, in his article on "Paper and Paper Standards," which originally appeared in SCIENCE PROGRESS, drew attention to this matter. He gives an easy and simple way of arriving at the relative durabilities of different papers by a few simple experiments, which I give in his own words:—

"1. Place the specimens each in a stoppered bottle containing a few c.c. of water. Set aside in a 'warm corner,' and after 10 or 14 days note what has happened. Papers of Class I.* will have proved themselves an excellent nidus for micro-organisms of all types. Colonies of these will have established themselves after their manner, and gorgeous effects in crimson, yellow, and blue will reward the observer. The filter paper (which by the way must not be allowed to come in actual contact with the water) will not show any such effects. They are obviously due to the nitrogenous colloid, the gelatine used in sizing the paper, for, as regards the cellulose fibres of which they are composed, the two papers may be considered as identical. Probably also the papers of Classes II.† and III.‡

* Class I.—Rag papers.
† Class II.—Chemical wood.
‡ Class III.—Mixtures containing mechanical wood.

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will not have grown any organisms. In other words, the pure celluloses are not susceptible to the direct attack of organisms. But, given a supply of the necessary nitrogenous and saline nutriments, they yield more or less readily in the inverse order of our classification. They yield, by undergoing hydrolysis, to soluble products allied to the starch sugar series, capable of assimilation by living organisms. The celluloses of the cereals and of esparto are very readily so attacked, and for this reason the tissue constituents of the straws are considerably digested in their passage through the digestive tract of the herbivora. Precisely for this reason the celluloses of straw or esparto rank very much below the normal or typical cotton cellulose as paper-making materials. The wood celluloses are intermediate."

The plan of suspending strips of paper of known composition in a stoppered bottle with water at the bottom but out of direct contact with the paper is very easy and very instructive. All paper may be said to contain the germs of putrefaction in a latent state, and the air is always teeming with them. When paper is brought into an atmosphere of this kind, and provided it contains sizing material upon which the organisms can start their growth, a change soon takes place. This test is a thoroughly practical one, and helps us to distinguish between different papers and their relative liability to mouldiness in such climates as prevail in parts of India and South America.

It may readily be seen that this subject is an important one to the stationer as well as the papermaker, as he should certainly know under what conditions papers are liable to destruction by organisms and other agencies.

It happens sometimes that papers are used under conditions which would give rise to the growth and development of these organisms, and under such circumstances, substances should be added to the paper in the form of antiseptics to prevent such growth if possible, but, better still where practicable, an attempt should be made to use papers which do not contain sizing material liable to putrefaction.

As regards modern means of applying antiseptics to paper, this subject belongs to the domains of the bacteriologist and the chemist. Thanks to the brilliant researches of some of our leading scientists, the power of many substances to arrest putrefaction has been largely, if not exhaustively, investigated. As many of these substances are, if not carefully applied, not safe to handle, I should hardly like to prescribe how and under what conditions such substances should be used, although I have

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had considerable experience with many of them. Chemists who have studied the matter can prescribe when the specific requirements are made known. There are many different treatments. For instance, we may want to treat a tub-sized paper so that it will stand the Indian climate, or we may want to go further and treat a paper so that it may be used as an antiseptic bandage, and not only be sterile in itself, but have the power of arresting or destroying the perishable matter with which it comes in contact. The questions naturally arise: How and where is the substance to be applied to the paper or stuff? What stuff and ingredients should be used? What antiseptic should be used, and in what quantity to give the desired result?

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LECTURE X. (Part I.)

SUNDRY PHYSICAL QUALITIES OF PAPER.

The Society of Arts Committee—Their decision—The acid action of drawing papers—Influence of rosin and gelatine sizing on strength—Deterioration due to mechanical wood—The lasting qualities of other fibres—Composition of blottings—Effects of moisture and heat upon expansion—Discoloration of papers by sunlight.

THE chief information we have on the subject of deterioration is contained in a report issued by the committee appointed by the Society of Arts to consider the question. This committee made a thorough examination of various papers used in this country with a view to adopting certain standards of quality and making certain recommendations not only to papermakers but also to those who are responsible for the uses to which paper is put, namely, the stationers, printers, publishers, the learned societies, and last of all, the general public. In passing I would briefly refer to the responsibility that rests chiefly with the publishers and printers of literature required to be of a lasting nature. With literature "which to-day is and to-morrow is cast into the oven" there is no responsibility beyond the exigencies of the moment, but it is important if not essential that the users of paper especially should know something of the transient nature of our modern and cheap papers; they should also know what papers will last and under what conditions such paper will stand the test of time. The information on this subject is at present very incomplete, but I shall do what little I can to give information bearing on this point within the short space of this lecture which would be of service. The report of the committee of the Society of Arts was published in 1898, and since that date other facts have come to light which might have modified the committee's opinion. There are, however, various points which deserve our serious consideration, and to which I will briefly refer.

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It is pointed out that actual disintegration has been proved to exist in papers of all grades, from rag papers to those of the lowest quality, but it is a question not only of material but also of conditions under which the papers are exposed. There are certain destructive influences at work apart from the ordinary wear and tear.

A great deal of the damage to papers is the result of exposure to an atmosphere where gas is used. The products arising from the gas give off sulphur, first of all in the form of sulphurous acid, which is afterwards oxidised to sulphuric acid. This, in contact with the paper, may bring about disintegration, even in the finest qualities. Then we have the question of a discoloration, which takes various forms, but is largely due to contact with air and exposure to light. In the case of papers containing such products as mechanical wood, this produces oxidation, and results in a darkening, especially in the edges of a book, which are more exposed to the atmosphere.

In all papers acid bodies appear to be formed as a result of oxidation.

The committee suggest that as rosin is the cause of the deterioration, as little rosin should be used for the purpose of printings as is practicable, and that it should not exceed 2 per cent. It is a well-known fact that bodies of the nature of rosin, if contained in large quantities in a paper, will bring about its disintegration, even if the fibres consist of pure cellulose. This is exemplified particularly in paper such as tracing paper, which contains a large proportion of substances of a resinous nature.

Then the question of what is known as acidity is an important one. It is a question whether papers may be finished with a slight excess of alum, which gives to the paper an acid reaction with litmus but is neutral to methyl orange.

The question of the so-called acidity of papers came to the fore when Professor Hartley announced to the Chemical Society that the acid reaction of litmus in Whatman's drawing was due to the presence of sulphuric acid as a residue from souring in the course of manufacture.

After this I studied the question and tested these drawing papers most carefully with different indicators, and contributed a paper to the Chemical Society, showing that the so-called acidity of these papers was not due to the presence of free acid at all, but that papers such as Whatman's gave, necessarily, a red coloration with litmus, that this red coloration is not the result of free acid,

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as proved from the fact that the papers give a basic reaction with methyl orange.

I have already treated of this subject at some length in a previous lecture, so that further reference is not needed here.

It is important that the papers should not contain an appreciative quantity of chlorides. Some chlorides appear to be harmless, but others are liable to decomposition and do a considerable amount of harm. The committee also draw attention to the question of colour. There is great danger when materials are over-bleached, as the bleaching action has the effect of rendering the material susceptible to change by atmospheric influences. Rag might be rendered as susceptible to atmospheric influence by bleaching as esparto is in the ordinary course.

After careful consideration, the committee came to the conclusion that 10 per cent. should be the maximum quantity of mineral used in papers and publications that are required for permanent use.

They were, no doubt, justified in this recommendation, which certainly ought to be acted upon, because it is now an acknowledged fact that mineral matter in excess reduces the life of papers.

The findings of the committee are as follows—First, normal standard of quality for book papers required for publications of permanent value. For such papers they would specify as follows—

FIBRES. Not less than 70 per cent. of fibres consisting of cotton flax or hemp.

SIZING. Not more than 2 per cent. rosin, and finished with the normal acidity of pure alum loading.

LOADING. Not more than 10 per cent. total mineral matter.

After the committee's report are given a number of abstracts from papers bearing on the subject of deterioration and allied subjects. These are mostly contributions by Herzberg. I will briefly allude to one or two of the more important conclusions arrived at, which, I think, in the main will be of interest both to papermakers and to stationers.

One important point is the influence of gelatine sizing on the strength of papers. A number of papers consisting of linen, hemp, and cotton fibres with 1.5 per cent. of rosin sizing were coated with one, two, and three coats of gelatine respectively. The results show that the breaking length and elasticity were noticeably increased by repeated sizing.

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In a further series it was found that the breaking strain was increased by successive sizing up to four treatments. Beyond this number it remained slightly below its maximum. The paper of the fourth treatment with size was 1.7 times the strength of the unsized paper. The elasticity reached the maximum of 1.8 times the elasticity of the unsized paper with the first sizing.

Of course, one must not draw the inference from this that paper tub-sized in the web gains in strength to the same extent, nor is it conclusive that all the additional strength is due to the gelatine. Much wetting with water alone repeatedly and loft-drying would tend to improve the strength of a paper.

The same water-leaf paper was also treated with size and starch and the results shown were very similar to those shown with the gelatine-sized paper. It seems fairly conclusive, therefore, that all papers are increased in strength as well as in their elasticity by tub-sizing, and I think this is a general experience of the practical papermakers. The starch trials have not much practical value, as starch is applied not to the web but to the pulp.

With rosin sizing, on the other hand, the results obtained by Martens show a very different result. They all show a lower breaking strain than the papers of similar composition, but without the rosin. It is concluded, therefore, that rosin sizing diminishes the strength and elasticity of mechanical wood papers. I believe that Hoffman, in his treatise on papermaking, also makes the same statement.

In order to test this treatment I made a series of tests with mechanical wood containing different portions of rosin, and instead of basing my conclusions on one or two samples, I prepared 30 or 40 mixtures and carefully tested them all, and compared them with a number of mixtures made without the addition of any rosin size. These results were published in the PAPER-MAKER. It is needless to refer to them in detail, but at first sight they do not appear to confirm the results, or rather the conclusions, of other observers. But I was working on paper containing 100 per cent. of mechanical wood. I think it is not difficult to explain the difference in the two sets of results. If the paper is very weak, rosin is capable of giving it additional strength, and the additional strength that rosin can give is partly dependent upon the amount used, but, unless the paper is very weak the rosin has no power of adding to its strength. Martens' statement that rosin sizing thus diminishes the strength and elasticity of mechanical wood pulp papers requires to be qualified. With certain papers, as for instance the mixture of mechanical

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wood and with a small amount of sulphite, the rosin may exert no influence, either one way or the other, upon the strength, but if the stock is further strengthened by the addition of more sulphite, the rosin is found to have a retarding effect upon the strength. Martens' statement that a certain paper when sized with gelatine shows a marked *increase* in strength with increased percentage of mechanical wood, but the elasticity diminishes, rather confirms my view that both rosin and gelatine have strength-giving qualities. Gelatine, being much the stronger of the two, would exert a much greater influence on mechanical wood paper than rosin would.

It becomes, therefore, a question of the relative strength or strength-giving qualities of the fibres of which paper is composed and of the sizing material.

It comes to this, therefore, that the strength of the paper is the mean strength of its ingredients. If you add gelatine to the paper and the strength-giving qualities of the gelatine are greater than that of the fibres of which it is composed, the ultimate strength of the sized paper will be somewhat greater than the waterleaf. If the waterleaf is composed of material which is very weak in the first instance, it is natural that the effect of gelatine should have an enormous increase upon its strength. Rosin, as we know, has much less strength-giving qualities than gelatine, and consequently when rosin is added to size papers composed almost wholly of mechanical wood, there is only a slight increase in strength, but when the furnish contains more sulphite fibre there is a slight diminution in strength with rosin, although an increase with gelatine. This explains the apparent contradiction between my own and Herzberg's conclusions. I do not wish to doubt his figures, only his general conclusions.

Martens gives some very interesting figures with reference to the effects of glazing on the strength of papers. His figures show that there is an increase of from 8 to 9 per cent. in the strength of the paper after glazing, and that this increase takes place in a similar manner whether across or in the direction of the web, and that there is very little difference between heavy and light glazed papers in this respect, but instead of an increase of elasticity as a result of glazing, there is an actual diminution of from 8 to 11 per cent. This is what one might expect on a paper that has been compacted by glazing.

A paper which bulks fairly well should have a greater elasticity than one which is very much compressed. He does not

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state what kind of glazed surface he used. The effect of plate glazing, especially when the material has been crushed by over-pressure, is very well known to papermakers. It materially reduces the folding qualities, so much so that when a sheet is sharply folded it very often cracks. This, of course, must be avoided, especially for papers manufactured for the making of envelopes. This is generally the result of over-pressure being applied to the glazing rolls, or the passing of the stack too many times between the rolls.

The Society of Arts committee do not appear to have drawn any attention to the effect which glazing or over-glazing have upon the ink-bearing qualities of the papers. Some papers are, I believe, often very much lessened in their ink-bearing qualities after glazing.

Martens states that in discussing the durability of printing paper in the present day, it has been proved that the daily papers have been printed on paper which rapidly becomes yellow, and he attributes this to the use of mechanical wood pulp. He furthermore asserts that three other new materials used in paper manufacture—wood, straw cellulose, and esparto—are believed to possess similarly bad characteristics, but states that they have been in use too short a time for any certainty to exist as to their durability. Anybody who has had the experience with straw and esparto will know that they are nothing like so perishable as mechanical wood pulp, although they are more perishable than chemical wood pulp.

The fact is that they are practically speaking oxy-cellulose, and behave towards atmospheric influences much as over-bleached cotton pulp would do. The durability, as far as we know, might be stated as follows:—Mechanical wood pulp, straw, esparto, chemical wood pulp, linen, cotton, *cæteris paribus*, mechanical wood being the least and cotton and linen the most durable.

We have now a proof that chemical wood pulp, if carefully prepared, is a material not far short in durability to cotton an linen, but no paper has been made a sufficient length of time for us to state with any degree of certainty how chemical wood pulp will stand the test of long storage and use, say over 200 years.

Herzberg's examination of papers made from sulphide cellulose showed that in ten months the paper possessed a slightly higher tearing strength, but that it had lost considerably in elasticity. Martens further emphasises the fact that for all publications of permanent value cotton and linen fibres alone should be used.

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Herzberg gives some interesting figures in regard to the trength and elasticity of samples taken from different parts of the ame sheet. He shows that there is specially a variation in the ase of paper made with long fibres, and with heavily loaded apers, but all the variations are found to obey no law, and to e purely accidental in occurrence. With strong papers made vith long fibres he found about 6 per cent. variation in the lasticity test and about 3 per cent. in the tearing test.

An interesting account is given by Herzberg in 1893 of a wood pulp paper made in 1852. From his statement it would ppear that so long as the paper was kept away out of the action f air and light it remained to all appearances unchanged. But lthough it appeared to be unchanged, it might be said potentially o have changed in some way, because strips of paper exposed to lirect sunlight for a period of 20 hours showed a decided change n colour. This would hardly have occurred with chemical wood ulp freshly made.

In 1894, Herzberg gave particulars of English, German, and French blotting papers, and the mode of testing them for their ibulous properties, as proposed by Winkler. This is based upon he height to which water will be drawn up by a strip of paper in definite period of time, when the paper is suspended vertically, with its bottom edge just touching the surface of the water. The strips were 15 mm. broad, and the time allowed was ten minutes. He divides the paper into two classes. Those which draw up over 100 mm. and those which draw up over 60 mm. At that date the English blotting papers showed very much the best results, the German and French being much inferior in bibulous qualities.

As regards the presence of mineral matter, this seems to be less important than it was commonly supposed in its effect upon the absorbent qualities of blottings, although the best qualities of all contain little or none.

It will be interesting to note at this date that all the papers examined, with the exception of two, were made of cotton fibres alone.

A further examination of blotting paper was made in 1896 of a much larger number. The mode of testing was the same, althought the results were expressed somewhat differently. In this series the English makers did not show up to the same relative advantage. The tests showed a great improvement in foreign makes, as compared with the English, and a change in the composition of the blotting papers made. Out of 89 papers, 42

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were made of cotton fibres alone, whilst the remaining 47 contained in their composition more or less of the following linen, wool, wood. In one case mechanical wood pulp was noted

It appears now from recent samples which have been submitted to me that papers of most excellent bibulous qualities can be produced from linen alone, and also from a certain class of wood pulp, if the same are carefully and suitably treated.

We next come to the question of physical change and alterations in papers by heat and moisture.

The question was studied by G. Dalén. The conclusions to be drawn from his tests are as follows:—That for percentages of moisture between 0 per cent. and 80 per cent. of saturation paper increase in length in direct proportion to the amount of moisture present. But when the degree of moisture ranges between 80 per cent. and 100 per cent. the expansion is somewhat over proportion. The longitudinal is less than the transverse expansion.

The effect of temperature is less than that of moisture favouring expansion when associated with percentages up to 65 of saturation, but retarding it beyond that degree.

Furthermore, there appears to be no permanent linear alteration in air containing less than 80 per cent. saturation. Under ordinary conditions the question of temperature for all practical purposes is by no means an important one, because we only use paper up to a temperature of say 90° Fahr. in the English climate. The results with higher temperatures, therefore, are of scientific rather than practical value. With moisture, however, it is different, as we often have very moist atmospheres and near the point of complete saturation.

Next we come to the question of the effect of sunlight on the size contained in paper. This has a direct practical bearing, but I venture to think that we must accept the statements made by investigators on this subject with a good deal of reserve. I will however, give you Herzberg's opinions which he expressed in 1896:—He exposed papers, both rosin and gelatine sized, to the action of sunlight, covering certain portions. At the end of the experiment the covered parts of the rosin-sized paper proved to have kept their size, whilst that exposed had lost it. Both the covered and uncovered parts of the animal-sized papers had deteriorated. This proves, he says, that in the case of rosin-sized papers it is light which causes the deterioration, but with animal sized papers it is some other destructive agent. He finds no loss of size either with gelatine or rosin papers on exposure to

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temperature approaching that of boiling water for a sufficient length of time to disintegrate the fibres.

It is supposed that the rosin on exposure to the sun is either destroyed or converted into something else. It certainly is not extractable by ordinary chemical solvents. Rosin size, even when sealed up, I know from long experience, changes entirely on exposure, and becomes insoluble. A lump of rosin will become pulverised. Added to this we have the fact that the rosin has a deleterious and weakening effect upon even rag paper on exposure, which shows rosin to be a very fickle substance under such conditions.

Herr O. Winkler, of the Leipsic Paper Testing establishment, has made a study of the action of air and sunlight on printing papers free from wood, the results of which were published in 1893.

He made cuttings of the cellulose and cellulose papers and exposed them for some days during the month of May to direct sunlight. Other cuttings were hung for 24 hours in the vapour of nitric acid and then treated with ammonia.

Winkler employed this method for some years to ascertain the tendency of paper to change colour and become brown on exposure. A more or less pronounced change takes place in the whiteness of papers free from wood after they are saturated with rosin size and submitted to this chemical treatment. The presence of the size seems to degrade the colour. It has been established that atmospheric air has no influence on the colour of pure cellulose paper unsized and free from wood.

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LECTURE X. (Part II.)

SUNDRY PHYSICAL QUALITIES OF PAPER (*continued*).

H.M. Stationery Office contracts—National Physical Laboratory—Work in Italy—Banknotes—Work in United States and Sweden—Climatic and local conditions affecting requirements—Drawing papers—Improvement on storage of papers—Effects of time on stretch and strength—Question of bulk—Influence of glazing on bulk—Effects of mineral constituents on bulk—Influence of glazing on appearance—Action of light on papers—Transparency—Opacity—Methods for determining opacity—Necessity for a uniform method.

I am indebted to Mr. E. Stallybrass, assistant examiner of paper to H.M. Stationery Office, for information in regard to the requirements of the Stationery Office for certain classes of paper.

The method adopted by the Stationery Office, although very different to the recommendations made by either the committee of the Society of Arts appointed in London or the Government testing stations at Charlottenburg, appear to me thoroughly practical, if not scientific.

With class 2 of the "schedule of papers required for stock," which are "writings, air dried," the mean breaking strain and mean stretch required are given for each paper. The figures represent the mean results obtained for both directions of the sheet, and are calculated on a strip of paper *five-eighths of an inch wide*, and having a free length of seven inches between the strips. By specifying the mean breaking strain as well as the mean stretch required on a given width, with a given distance between the clips for this class, the Stationery Office can ensure having papers answering to these special requirements, at any rate the conditions of the test, a specific which is more than can be said of the German method.

Class 3 are ordinary writings, machine made, animal tub-sized, but there are no special requirements as regards strength and breaking strain specified, except with tobacco band paper, where it is stated that, this paper being required for printing from the

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plate, it is essential that the sheets should be uniform in texture and free from fibre-knots and other hard particles.

Class 5.—Blotting papers. Specified to be all rag, machine made, and free from loading.

Class 6.—Printing and lithographic papers. General specification, rolled, machine made, engine-sized, loading not to exceed 15 per cent.

Certain of the papers of this class are required to be free from stretch when used for colour lithography.

Class 9.—Brown papers, *air-dried.* Specification, air-dried, machine made. For this class the mean breaking strain and mean stretch required are given for each paper. The figures represent the mean of the results obtained for both directions of the sheet, and are calculated on a strip of paper *two inches wide*, and having a free length of seven inches between the strips. In case of papers indicating a higher breaking strain than the minimum required, a proportionate increase in the stretch must be shown.

Note the difference between the width of the strip in this case and the previous one cited.

I am informed that the reason for insisting upon a strip of two-inch width here is that it is found by experience that for the coarser kinds of paper, such as browns, which always contain thin spots, a five-eighth inch strip is not wide enough to get a fair idea of the general strength. The result is that a narrow strip will only indicate the strength of the thin spots, which is by no means a fair criterion of the general strength of the paper. It is not thought that within certain limits these thin papers, when surrounded by thicker portions, materially detract from the strength of the paper when in actual use. These considerations have led H.M. Stationery Office to take a wider strip for this class of paper.

Class 10.—Brown papers, *cylinder-dried.* General specification, machine made. As regards the length and width of strip for taking the breaking strain, this is the same as for class 9; but note that it differs from that class in that no "mean stretch" is specified, and for this reason it is found that the stretch of a paper is to a great extent an index to the amount of handling it will stand. One paper may show a much greater breaking strain than another, and yet may not stand nearly so much handling. This would be due to the latter being more elastic. As class 9 papers are required to be practically durable. it has been found advisable to specify the stretch. Class 10 papers are used when

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great durability is not required, and it has not been found necessary to specify the stretch.

For fine papers, on the other hand, such as class 2 above referred to, it is considered necessary to have a uniform thickness all over the sheet, and thin spots are a decided drawback, hence it is that narrower strips are specified for the strength test.

Chemical wood must not be used in the manufacture of any papers with the exception of engine-sized coloured printings and buff papers, where an addition up to 25 per cent. will be allowed. All animal tub-sized papers are required to be as far as possible free from earthy matter, and, except where specially stated, the amount of loading added to other papers must not exceed 6 per cent.

When sulphite or soda wood are used either separately or conjointly in the manufacture, the quality of neither material shall separately exceed 50 per cent.

I am furthermore informed that for documents which are required to last as long as possible, such as certificates of births, deaths, and marriages, &c., the Stationery Office adhere to hand-made paper.

For documents of next importance are used air-dried and tub-sized paper made entirely of rags.

For Blue Books ordinary printings are used, which, however, are required to be free from chemical wood, and not to contain more than 15 per cent of loading.

The Stationery Office have a particularly strong hand-made loan paper which is used for documents which are subjected to a good deal of handling, such as tickets of leave.

The "National Physical Laboratory" has recently been established at Bushey House, Teddington, by His Majesty's Government for standardising and verifying instruments, for testing materials, and for the determination of physical constants. The laboratory is intended, like the Riechsanstalt in Berlin, to have the authority of a national institution, and does not seek to interfere with local institutions.

I am indebted to the director, Dr. R. T. Glazebrook, F.R.S., for information as to what is contemplated as far as paper is concerned. In the physical department the testing work includes, among other experiments, No. VIII., "Chemical and Microscopic Tests of Papers and Similar Materials."

I am informed that the National Physical Laboratory are making arrangements for the ordinary chemical and microscopical examination of papers of a good class, and this will be extended

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to papers of other classes if there seems to be a demand. The tests will be undertaken for a fixed fee.

An interesting series of articles has recently been translated from the Italian and published in the PAPER TRADE REVIEW, dealing with the preservation of Italian State papers, and giving the official tests, by Dr. Scavia in REVISTA TECNICA.*

He states that, notwithstanding the remarkable progress made during the last 30 years in the machinery and chemistry of the paper industry, there has been a general decline in the articles manufactured, especially from the point of view of durability. With this remark I think most people will agree. He quotes Professor Loevinson:—"Lamentable experience demonstrates continuously that light of too great intensity or humidity, cold, and insects, in addition to the use of inferior qualities of size and materials for bindings, are the most inveterate enemies of those printed and written documents which should resist as long as possible the injurious action of time."

Dr. Scavia states that "The continuous deterioration of printed and written documents, the consequence of utilising such a quality of paper, which can also be demonstrated by chemical tests, would necessarily lead to complete and irreparable decay at a more or less distant time."

An account is given of the work aided by the Turin Chamber of Commerce, working for the object to which it owes its existence—for analysing and testing different kinds of paper, raw materials, &c.—and it is stated that in addition to a description of the different appliances used for testing, a small plant was installed for experimental and educational work to make hand-made paper.

"It is not a question of adopting normal types of papers bearing appropriate figures and water-marks like a normal 'papier' in Prussia. †*We must not place useless difficulties in the way of industry, nor suddenly shackle it by a regular disciplinarian system.* It is merely requisite to study the various current types of paper employed by various administrations, examine their defects from the point of view of durability and resistance, and fix a technical data with which the new paper should comply, within certain limits, in tests at the government laboratory."

This is somewhat awkardly expressed, but the meaning is very clear. I think we must agree that the German system is far too rigid, or shall I say impracticable? It does not appear that normal papers are required so much as a practical system of

* See PAPER TRADE REVIEW, Vol. 38, Nos. 14, 15, and 16.
† The italics are mine.

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testing. His Majesty's Stationery Office have adopted a practical system (as above described) in a few instances, but the system needs to be extended. These tests should not hamper the paper-maker, but merely be the means of compelling him, or I would rather put it, aiding him in keeping up a certain standard of quality, sufficient merely for the purpose for which the paper is used, and as a safeguard to the stationer and printer, who have a right to know something of the composition and physical properties of the paper they purchase.

In the table communicated by Dr. Scavia, showing the various papers used for particular purposes and their compositions, the rag papers certainly show the best results, not only as regards breaking strain, but also as regards resistance to compression. It is pointed out that the effects of such tests would be that the Government would buy an article on such tests and not on the system of manufacture. It certainly does seem that what should concern the buyers most is the quality of the paper and not the system of manufacture.

As regards the conditions for drawing papers, it is stated that the paper must not have an alkaline reaction; but a very slight acid reaction with blue litmus can be tolerated, provided that this is due not to acids but to neutral salts which change the colour of litmus. Elongation must not be more than 6 per cent.

The same translation in discussing the special methods and qualifications of banknotes in different countries, and the means adopted to prevent fraud, states: "Amongst nations and institutes which give, so to speak, equal importance to printing and paper, Russia is the chief. The Russian type of banknote may be regarded as the most perfect in existence."

From experiments made with various kinds of notes, it is considered that, with due regard to what has been said, a good type can be obtained, especially small notes, when the following conditions are fulfilled:—

Average rupture strain ..	8 to 9 kilos.
,, ,, length ..	6,000 to 7,000 m.
,, elongation per cent.	9 to 11.
Percentage of ash	Less than 3.

Resistance to crushing with 3,000 to 5,000 revolutions of the Schopper dynamometer and a strain of one kilo. on the springs.

A test of crushing "notes" gave the following results:—

Average rupture strain ..	5.04 kilos.
,, ,, length ..	4,318 m.
,, elongation per cent.	6.29
Percentage of ash	2.43

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As regards what the various countries are doing for the establishment of tests there is not much information available. Germany we know all about. I have already referred to what little is being and has been done in this country, and we have just spoken of Italy.

It is not unlikely that the United States will give us a lead. It is reported from Washington, D.C., that the Bureau of Forestry has established a testing office in co-operation with the Bureau of Chemistry. Particular attention will be given to the study of woods; also a study has been planned of the composition and physical characteristics of the various papers containing either mechanical or chemical wood pulp which are found on the American market. The ultimate object of this work is the establishment of a paper-testing laboratory similar to that now being operated by the German Government at Berlin. The necessity of such a laboratory is apparent when it is considered that practically all official publications are now printed on such paper, and that the life of wood pulp papers is, in general, very brief. The importance of certain standards is self-evident, and it is hoped to establish and enforce these for American papers, at least where they are furnished to the Government.

I have it on good authority from a large firm in Sweden that there will be in the near future new regulations with regard to the manufacture of paper for the Swedish Government. The promised new regulations are to a great extent in accordance with the old German standards, and allow the use of mechanical and rosin-sized paper even for documents that ought to be of unlimited durability. I have been engaged on behalf of a large firm in Sweden to report upon the whole subject. It is to be hoped that the Swedish Government will safeguard themselves against inferior qualities for permanent documents.

The question of paper standards or standard methods for the examination and testing of papers for different countries requires a knowledge of special circumstances and conditions. The question is affected by climatic conditions. In a hot and humid climate it is absolutely necessary that something should be added to the paper to prevent its putrefaction. In England this can hardly be said to be the case. Papers have to be specially prepared for the Indian market. Then, of course, the question of the individual requirements of the country have to be taken into consideration.

But I do not wish it to be inferred that papers always tend to deteriorate if kept for any length of time; fortunately the

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reverse is the effect in certain instances. Some papers are very much improved by keeping. A more exact knowledge of these improvements, as well as conditions which effect changes in papers resulting in improvement, should be very helpful to the buyers and sellers of papers. This subject was discussed in the columns of PAPER AND PULP, in the correspondence class which I conducted this year.

The leading water-colour artists know what they want in the way of paper, but they find that they do not always get what they want. Some years ago when this controversy was going on about the so-called acid action of drawing papers, I was invited to the Savage Club to meet one or two well-known men who volunteered to give me their experiences and state their requirements, with a view of influencing papermakers to produce what they wanted.

It is a well-known fact that certain drawing papers of certain dates by a well-known maker are very much prized by artists. A well-known artist informed me that this improvement is in what is technically called the "tooth" of the paper and is the result of ageing. In this case we have an improvement in the surface of the paper which is brought about by ageing or stocking, but it is evident that papers even of similar composition age differently, because the makes of some years improve on ageing, whereas the makes of other years do not, at any rate to the same extent. This appears to be an uncertain quantity, very much like the ageing of wine.

Gelatine papers, especially those which are dried hastily, are also improved considerably in many instances by keeping in stock, during which time the gelatine, which should finally contain about 17 per cent. of air-dried moisture, resumes its atmospheric condition. This improvement can be better realised by noting the effect of moisture upon a sheet of gelatine. The gelatine in a dry air or if placed in the sun is liable to become very brittle, but on removing it to an ordinary atmosphere in the cool it resumes its strength and toughness. The same undoubtedly takes place, in a measure at any rate, in regard to the microscopic films of gelatine in tub-sized papers.

Many papers, such as "browns," improve both in feel and strength and general qualities when kept in stock. I believe it is not an uncommon thing for a buyer of paper to reject browns and return them to the mill as not being up to sample, but on the same parcel being tendered to him a few months later, he has been known to accept the paper and find it perfectly satisfactory. This is the result of a change which has taken place in the paper

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itself, partly due to the paper becoming restored to its natural condition as regards moisture, but especially owing to the fibres settling thenselves down and a certain amount of expansion or contraction taking place in the paper itself, as it settles down to its normal condition, resulting in the final production of a more natural sheet. This is by no means an easy question to explain, but from general experience it has become a well-known fact.

I would suggest that the following conveys a better idea of what change or changes take place under such conditions. A machine-made cylinder-dried brown is essentially, as the name conveys, an artificial paper, *i.e.*, the felting, stretching, and drying are done under conditions that are not at all natural to the felting and drying of the fibré. It results from this that the fibres of paper so produced are in a state of tension, and attempt to resume their natural shape and position. On storing, this paper takes up moisture and the fibres by slow degrees draw into their natural positions. The result is that the paper is often much improved in strength, feel, and surface, although common experience seems to indicate that the stretch is often diminished with some printing papers.

The following results quoted by one of those who entered the correspondence class instituted by PAPER AND PULP show an improvement in the breaking strain due to storing for 10 months, accompanied by an increase in weight of 3 per cent., although it shows a diminution in the breaking tension. This confirms the opinion of a previous investigator.

"I once tested a tub-sized paper for strength and then carefully rolled the sheets and laid them on a high shelf where air, but diffused light only, could reach them. *Ten months* later I again tested them. The following are the figures:—

	ORIGINAL TRIAL.	SECOND TRIAL.
Breaking Strength.		
Average Dn. and Ac. Mc.	3.781 km.	4.145 km.
Breaking Expansion ...	5 %	3.6 %

Increase of weight = 3 %"

As regards the loss of finish or storage, it is remarked by one writer that:—

"On the other hand, M.F. papers, if kept long in stock, especially in a cool room, will go back in finish owing to the fibres being expanded. [In this connection I might say soft-sized papers will lose their finish quicker than hard-sized, and printings quicker

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than writings, the presence of the size, especially if it be rosin, preventing an undue amount of moisture from being absorbed. The colour also will fade, and the sheet will have a "*dulness*" which newer ones do not have. The colour will fade more rapidly in seaside places, due, I suppose, to the larger quantity of oxygen in the air acting in conjunction with moisture.]

"All papers on absorbing moisture stretch a little in both directions, *i.e.*, along the direction of the web and across, but principally across. Therefore if a paper is lithographed without being properly matured it runs a great chance of stretching during the interval between the impressions, throwing the final impressions out of register.

"Note direction of curl, which invariably takes place parallel to direction of web."

The improvement to envelope, litho, and printing papers is chiefly due to the equalisation of moisture as affecting their after-behaviour.

Envelope papers are improved by lying in stock, as this cures the tendency to "curl," which causes great annoyance to the envelope manufacturers when feeding the dies into the folding and gumming machines. The curling is due to the moisture from the air getting in at the edges of the sheets; if exposed a sufficient time the sheets will absorb the moisture uniformly all over the sheet and curling is remedied.

Newspapers and common printings are well known to improve by keeping for a short time, the paper working much better and taking the ink from the type easier, so as to produce a well-printed sheet. The reason for this is that the paper often leaves the machine too dry, and when in contact with the atmosphere for some time the paper becomes air-dried, or damper than when it left the machine, and damp paper always prints better than dry, absorbing the ink better.

The question of bulking, as affected by composition and treatment of fibres, is outside the scope of this lecture, but the question of reduction of bulk as affected by glazing might be briefly referred to as belonging rather to the domains of the finished paper. I give some results supplied during the correspondence class, as giving some idea of the reduction in bulk with different finishes. These figures would of course vary considerably with different finishes and compositions; they give some idea, however, of the effects of compression upon paper. The following are the results of four papers tested for bulk,

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all of same weight (30 lbs. demy, 480 lbs.), and same furnish including loading:—

		Thickness, 1=100.	Loss in thickness.
		%	%
1. Rough antique finished,	6.0 thousandth of an inch	100	0
2. Best machine finished	4.6 ,, ,,	76	24
3. Plate-glazed ...	3.8 ,, ,,	63	37
4. Super-calendered ..	3.5 ,, ,,	58	42

Other factors being equal.

The presence of clay affects the question of bulk. Mineral does not, at any rate as a rule, add to the bulk of a paper. If, therefore, you have two papers containing each, say, 10 per cent. of mineral, A 10 per cent. of clay, B 10 per cent. of baryta, each of them contains 90 per cent. of fibrous material, and if this fibrous material is the same for the two papers in every respect, the bulking of these two papers will be the same. Neither the clay nor the baryta add to the bulk, but simply tend to fill the interstices. The clay being of lower specific gravity than the baryta, and consequently occupying a greater space for a given weight, will fill the paper to a greater extent than the baryta, but neither will bulk the paper. I do not wish to assert that papers containing a very large proportion of mineral matter are not increased in bulk thereby, but within reasonable limits the mineral simply fills the paper and diminishes the air-spaces. Of course when you come to a paper heavily loaded, the air-space of which is largely closed by the mineral matter, it will not diminish in bulk to the same extent at the super-calenders as an unloaded one. This stands to reason from what has been already stated. Furthermore, it stands to reason that two papers, A containing 25 per cent. of clay and B containing 25 per cent. of baryta, B could be reduced in thickness more on super-calendering than A. All these points are of interest and of some practical moment, and a thorough mental grasp is a desideratum.

The behaviour of paper towards light demands special study. All papers may be said to be translucent, that is, they are neither completely transparent nor completely opaque, some tend in one direction whilst others tend in the other direction. This property of partly transmitting and partly reflecting light is characteristic of all papers. The character of the surface imparted to the paper would affect the question considerably. Supposing you plate-glaze a paper and crush it, you certainly would not get the same result as regards transparency as if you super-calendered it, or as if you friction-glazed it on one surface only. Each of these papers would be differently affected as regards the question of transparency. Some kinds of glazing may be said to affect only the

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surface of the paper and not the interior. Plate-glazing may be said to affect the whole of the fibres.

Let us deal with the subject from the point of view of opacity, and endeavour to obtain an optical explanation of opacity of paper and see how it can be measured.

The fact that colour fades more quickly at seaside places may be due to the fact that there is a greater amount of ozone (not oxygen) in the air, combined with a greater amount of moisture. The amount of oxygen in the air, whether at the seaside or any other place, is practically constant, but the amount of ozone varies, and is greatest at seaside places, and as ozone is an active bleaching agent and requires a certain amount of moisture to give it its greatest activity, it is highly probable that the fading of papers at seaside places is due to this cause.

Rosin-sized Papers.—The action of light on rosin-sized paper gradually produces discoloration in proportion to amount of rosin they contain.

Discoloration.—The discoloration of "self-colour" papers is generally brought about by oxidation of the non-cellulose portion of the material, but with some rag papers where this was formerly thought to be the case it has been due to the excessive quantity of rosin used. This is acted on by sunlight, and a brown, sandy colour is produced. The formation of sulphides is a most objectionable feature with ultramarine coloured papers, and this combined with the action of alum causes the colour to fade.

You want some slight knowledge of the science of colour and optics. To gain the necessary knowledge you could not do better than read the little book by A. H. Church, on "Colour" (Cassell & Co.), also the little book on "Colour Measurement and Mixture," by Capt. Abney, published by the Society for Promoting Christian Knowledge, but if you find even these two books too much for you to understand, you need not be discouraged, because, although they are of very great value to a proper understanding of the subject, you can advance your knowledge considerably without them. There are one or two references in Church's book to the subject of paper. "When the rays of parallel light from the sun strike upon a rough, that is, an unpolished surface, say, of a piece of white paper, they are incident at all imaginable angles, with minute surfaces of the hollows and ridges which make up the reflecting substance, and such of them as are reflected obey the law, but are reflected in a countless number of different directions." This reflection of light in a countless number of different directions by the small fibres which compose the paper

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is the real cause both of the whiteness and opacity of papers. The greater these countless reflections the greater the opacity—the less the transparency. "The numerous small reflections which occur from and between the surfaces of the felted fibres in a piece of white paper may be greatly lessened by wetting or oiling the the paper, when it becomes less opaque, and at the same time greyer and clearer; to this cause the transparency of tracing paper and tracing cloth is due."

"Bodies are said to be transparent when they permit light to pass so freely as to allow objects to be perfectly discerned through them."

It is by no means the best way of testing the transparency of paper to hold it up to the light. Of course, if we hold two papers up to the light, the one which appears the lighter of the two is the more transparent. What we want, however, is some simple mode of expressing the relative transparencies of different papers, and some simple and rapid way of making the tests. I will briefly describe the method which I have made use of for this purpose. It is simple and does not require any scientific knowledge, and I think you would all have no difficulty in making use of it.

Take a piece of white opaque paper printed in black with block letters. If you take two papers, one of which is transparent and the other opaque, the letters will be more easily read through the transparent than the opaque paper. This method of comparison is of course different to holding paper up to the light. In the method I am describing, the light has to pass through the paper and illuminate it sufficiently so that the background is discernible. The light has to pass twice through the paper, first to illuminate the background and back again from the background to the eye. Now, suppose I take a number of papers of the same composition exactly, but of different weights per ream. Suppose for the sake of argument they are fairly thin and transparent papers. It is merely necessary to fold each a sufficient number of times so that it just renders the background invisible. Let us assume that A requires to be folded five times, B seven, and C eight. The one which is folded the greatest number of times is the most transparent, and relatively speaking we may compare the transparencies of these papers by stating the number of folds. The relative transparencies of these papers would therefore be five, seven, and eight respectively.

Now, suppose we take papers of different materials but of equal thickness, and desire to know their relative transparencies.

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We take a case in point. A is a linen bank and B is a sheet of tracing paper of equal thickness. We have to fold A five times and B nine times before we obliterate the image at the back. We are able to state that, thickness for thickness, the transparency of A is to B as five is to nine. If we desire another comparison, we can take papers of different compositions but of equal weights (demy). Now, of course, it does not follow at all that these papers will bulk equally, but a stationer may require to substitute one paper for another at so many lbs. demy. He may require a greater capacity. Now, we must assume again that these papers are fairly thin. A requires to be folded twice and B three times. From this we conclude that, weight for weight, the transparency of A is to B as two is to three.

Now we come to a further mode of treating the subject, and one which will enable you to come to very useful and definite conclusions from a papermaker's standpoint and throw a lot of light on the question we have been discussing, We have, for the sake of example, a number of papers of different compositions but made under known conditions. Let us assume that we wish to determine the influence of china clay on the question of opacity in an esparto paper. We know the ashes of the different papers; from this we can calculate the percentage compositions of esparto and clay. It is not necessary that these papers should be of equal thickness. We take each of them in turn and place them over the background as before, and then, by means of a micrometer, we measure the thickness of each paper necessary to extinguish the background. The one which measures the thickest is, of course, the one which is most transparent, and the one which measures the thinnest is the least transparent, thickness for thickness with the others. The micrometer readings expressed either in thousandths of an inch or in millimetres will express the relative transparencies of these different papers, thickness for thickness; and by comparing the compositions with these figures it will be very easy to arrive quickly at some definite conclusion. The same *modus operandi* can be used with regard to other mixtures and compositions. If the work is always conducted in a light room, but not in direct sunlight, one series of operations can be compared with the other on this basis. Such figures would undoubtedly be of great value in some mills where the question of transparency and opacity is of considerable moment.

I notice in the PAPER TRADE REVIEW, March 7th, 1902, an account of a method employed by Mr. O. Winkler for the deter-

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mination of the opaqueness of printing papers, which is very similar, although not identical with that which I employ. I am glad to see that Winkler thinks there should be some standard method of determining the opacity of paper, to be agreed upon by the buyers and sellers. The method such as he and I have made use of might very well be employed in ordinary commercial practice. Apart, however, from the employment of such a method by buyers and sellers, it would be of the utmost value to many manufacturers for making comparison of their different makes. The difference revealed to them by their different makes and compositions would assist them in determining in which direction to work both for opaque or transparent papers. Much of the difficulty now experienced by manufacturers is due to the roughness and looseness of their methods of comparison giving too much scope for individual bias, and introduces an uncertain and undesirable factor which chemists generally call the "personal equation." All tests for commercial purposes should be such as to eliminate, as far as possible, the "personal equation."

In concluding this lecture I should like to add that this branch of the subject concerns the papermaker and stationer alike, but has not yet received much attention. The information is fragmentary and scattered. In some cases the conclusions arrived at by different investigators are contradictory. The information at present savours too much of the scientist and too little of the practical man. What is wanted is systematic study and daily records, which in course of time will become yearly records. The records must be accurate, and care must be taken that conclusions must be arrived at only after plenty of records have been accumulated and carefully examined. The subject does not concern the present so much as the future. It is a subject which might well occupy the attention of the National Physical Laboratory, but I venture to think the large stationers and publishers of this country would do well to put someone to carry out a systematic series of researches, with a view all the time to attaining some practical object, and with a view to finding out exactly "where they are" with the papers that pass through their hands into those of the general public, and further with the view of ascertaining in each case the most suitable paper for each of the multifarious purposes to which paper is put.

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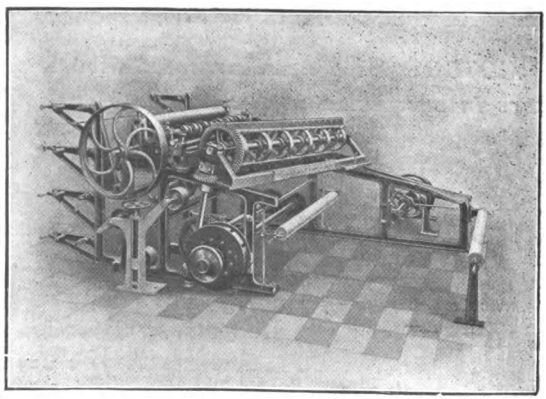

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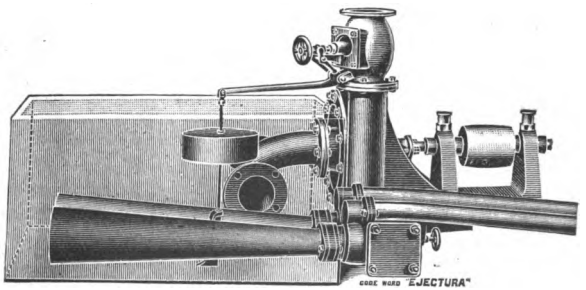

Two Centrifugal Pumps complete the whole Pumping arrangements of a modern Machine.

ABSOLUTE SIMPLICITY—POWERFUL AND CONSTANT VACUUM—WASHING UP MINIMISED.

The Users say they are the best thing that has been introduced to Machines for years.

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BERTRAMS' PATENT ROPE DRIVE.

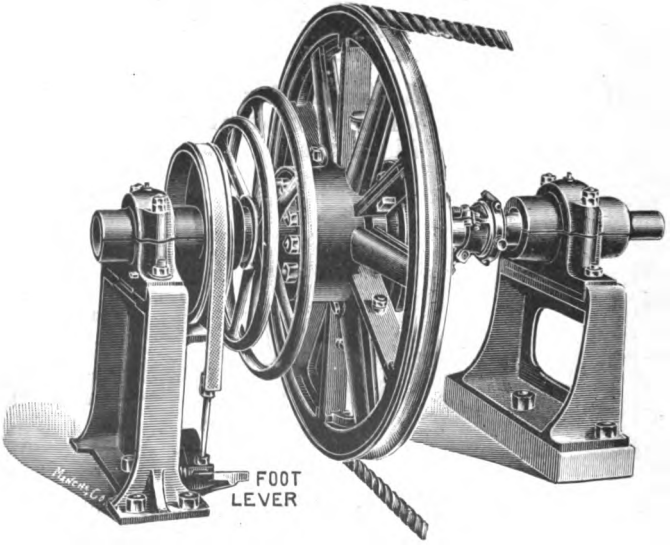
Gives thorough control of the draws of paper throughout the papermaking machine.

Absolutely regular and smooth running without any jerking motion.

Extreme simplicity of details, which simplicity is not lessened in the complete drive necessary for the largest machines.

Goes into the least possible space.

Only one rope needed to drive machine from couch rolls to reel.



PATENT EXPANDING ROPE PULLEY
FOR SECTIONAL DRIVING OF PAPER MACHINES.

Code Word "***EXPANSURE.***"

BERTRAMS LIMITED, ENGINEERS, SCIENNES, EDINBURGH.

Automatic stretching arrangement takes up slack of rope, and that when the rope is not under the tension of power exerted.

No cumbersome parts to lift or lower when stopping or starting any section of the machine, the stopping or starting of each section being effected without any skidding of a pulley on a belt.

No overhead shafts nor bevel gear necessary.

For a machine having say eight sectional drives, only 16 bearings are necessary on entire shafting from couch roll to reel.

Sole Makers: **BERTRAMS LIMITED.**

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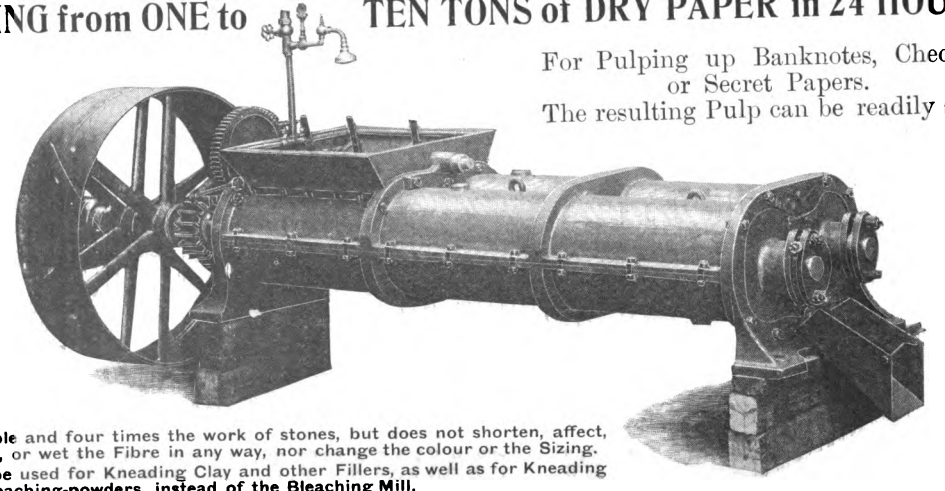
Dr. C. WURSTER'S PATENTED

"Pulping-Machines" & "Kneaders,"

For Pulping up Machine broken, Old Paper Stock, Waste-paper, and Dry Woodpulps.

PULPING from ONE to TEN TONS of DRY PAPER in 24 HOURS

For Pulping up Banknotes, Cheques, or Secret Papers.
The resulting Pulp can be readily sold.



Does double and four times the work of stones, but does not shorten, affect, **crease,** or wet the Fibre in any way, nor change the colour or the Sizing.

Can also be used for Kneading Clay and other Fillers, as well as for Kneading **Dry Bleaching-powders, instead of the Bleaching Mill.**

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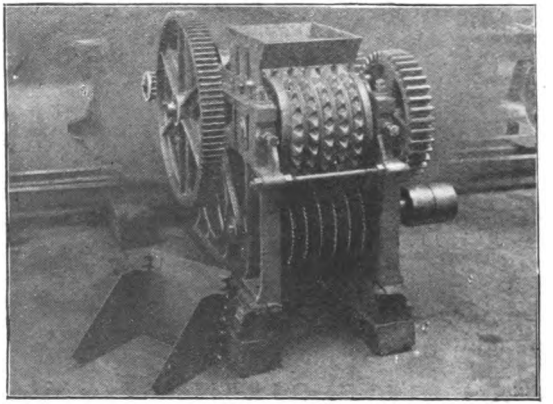
PAPER-TEARING MACHINE,



For destroying, by tearing up, Confidential Papers or Documents in the dry state, giving saleable old paper stock.

For tearing up machine broken, Paper Stock and Wastepaper, to be conveyed automatically to the Kneader, Stones, or Beaters. Very useful for Dry Woodpulps and Stock, where Propellers are used in the Beaters.

For full particulars apply to

DR. CASIMIR WURSTER, Dudley Mansions, 29, Abbey Rd., St. John's Wood, London, N.W.

For Re-agents for testing, and for the determination of Mechanical Woodpulp in Paper, apply to

DR. THEODOR SCHUCHARDTS, Chem. Fabrik, Görlitz.

For Small Hygrometer, apply to

W. LAMBRECHT, Göttingen, under the name of "DR. C. WURSTER'S Kleiderhygrometer."

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PATENT

Refining Engine.

AT WORK ON ALL CLASSES OF - PAPER, AND THE SIMPLEST AND - MOST EFFICIENT IN CONSTRUCTION.

* *

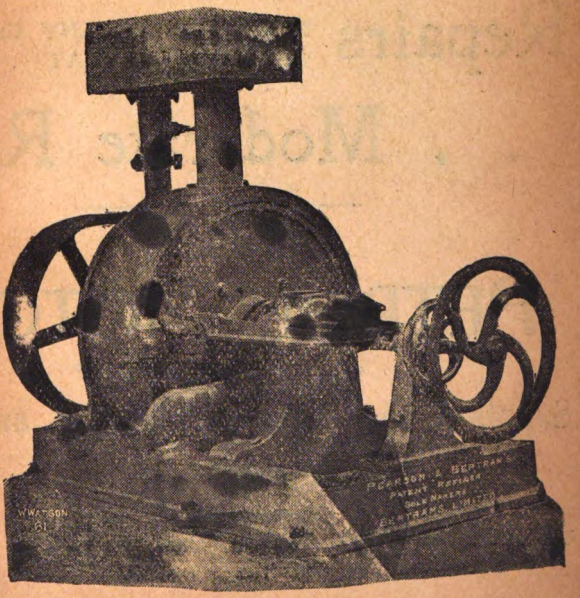
Greatly . . lessens time required for pulp in . . Beaters, and increases . output.

Makes closer wove and . clearer laid papers.

Reduces . . broke to a minimum.

Thoroughly . assimilates . all classes of pulp.

* *



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